SOME TOPICS IN SOLID STATE PHYSICS

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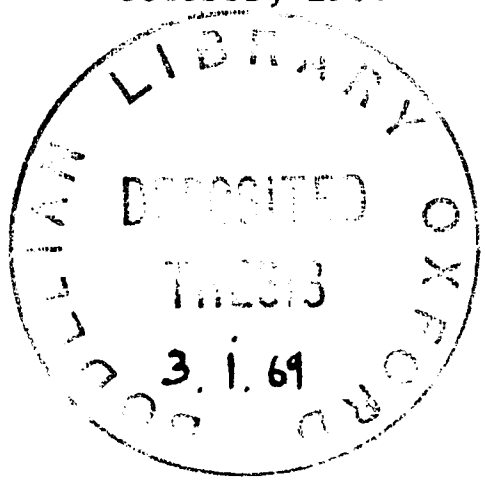

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ABSTRACT

The subject of this thesis is a theoretical study of some of the optical properties of crystals of CaF_2 and Si which have had atoms of different mass and chemical properties substituted for a small percentage of the host atoms. The low concentration of the defects enables each to be considered independently as a single foreign atom substituted into the crystal. The work divides into two parts, distinguished by the different structures of the crystals and by the different phenomena to be explained in either system.

In Si, with B^- or P^+ substituted in as defects, the problem of interest is the mechanism and intensity of optical absorption by the crystal. Since Si forms a covalent bond with itself, the pure crystal is homopolar, and does not absorb light. A charged defect will absorb in the normal way. However, in homopolar crystals such as Si, theoretical attempts to describe neutron scattering and other experiments have led to the rejection of the rigid-atom model in favour of the Shell model, which allows each atom a shell of outer electrons not rigidly attached to the nucleus. The effect of this is that the atoms are polarizable, and have an extra three degrees of freedom, associated with their electric dipole moments. In the case of a charged defect, there are now three absorption mechanisms: one due to the dipole of the oscillating charge itself; one due to the dipoles created throughout the crystal by the effect on the polarizable atoms of the changed

polarizability of the defect; and a final mechanism whereby the charge on the defect sets up a static electric field which induces dipoles on the polarizable atoms through an anharmonic effect.

The significance of this last mechanism relative to the others depends on whether or not the Lorentz local field correction is to be used. Using a version of the Shell model in which changes in the defect charge and polarizability can be included explicitly in the absorption, we show that this correction factor is always present, although it may be modified by changes in the defect polarizability. We are able to fit the experimental frequencies and intensities for the localized modes due to boron, and also for those due to carbon, using these changes as parameters.

Our calculation is based on the simple relationships between the absorption, the susceptibility and the frequency-dependent displacement-displacement Green's functions. The parameters used in the Shell model for the perfect silicon lattice are taken from experimental fits to neutron data for the dispersion relations.

In CaF_2, H^- and D^- ions have been substituted into F^- sites. These ions differ from F^- mainly in mass, and can be observed experimentally by absorption of infra-red light at 1.849×10^{14} ra/sec (H^-) and 1.323×10^{14} ra/sec (D^-). These figures indicate that the effect of the change of mass is reduced by a weakening of the force constants which bind the defect to the other ions in the lattice. We explain the changes in the above fundamental frequencies, and those of the harmonics, which appear when the crystal is subjected to uniaxial stress. The

stress causes the lattice to strain, and the effect of this strain on the anharmonic forces present is to produce new terms in the harmonic forces, which modify the frequencies. In particular, the weakened force constants at the defect allow additional relaxation of its neighbours, which makes the change in the frequency of the localized mode more pronounced.

We find the relaxation by a Green's function technique which inverts the force constant matrix, ϕ , of the perfect lattice.

The six force constants which constitute ϕ out to 3rd neighbours have been evaluated as parameters in a rigid-ion model which fits the elastic constants of CaF_2 and other experimental data. The changes in the central force constants coupling the defect with its 1st and 2nd neighbours are found by fitting the vibrational frequencies to the experimental data, and are respectively - 65% and - 22%. (It is also necessary to reduce the effective charge on the defect by 46% to get this fit.) Using the relaxation obtained, assuming that the defect vibrates in a static environment, and taking as parameters the central anharmonic forces coupling the defect with its 1st and 2nd neighbours, we derive expressions for the parameters of the phenomenological model which describes the frequency changes of the defect vibrations under stress. We thus evaluate some of the anharmonic force constants, and can show that a Lennard-Jones potential describes the behaviour of the defect to a fair approximation.

A useful sideline of this work is a derivation of the changes in the macroscopic ~~force~~ elastic constants of a crystal which contains a small concentration of defects.

CONTENTS

CHAPTER I

INTRODUCTION

I.1 The forces which bind atoms together in an insulating crystal are crudely understood on the basis of a number of models. These include electrostatic forces, homopolar binding (a quantum mechanical effect due to the exchange of electrons), van der Waals forces (due to the mutual polarization of two neutral atoms), and repulsive forces due to the Pauli principle. This understanding is crude due to the difficulties of calculating most of these forces, especially in crystals. Since first-principles calculations are still not possible, it is necessary to develop experimental and theoretical tools to further our understanding of the forces in crystals.

A certain amount can be inferred from the macroscopic properties of insulators, such as specific heat, elastic and dielectic constants. But these are not really meaningful until related to microscopic models. Much more information is provided for testing such models by optical spectra and by X-ray and neutron scattering from very pure crystals. In recent years, a new tool has been made available to experimenters through the study of optical properties of defects in the crystal. This thesis is concerned with some aspects of point defects vibrating in a lattice.

The defects we are concerned with consist of foreign atoms substituted for one of the atoms of the host lattice. They are charged, thus giving rise to optical absorption when they vibrate. The frequency

and amplitude of this vibration can be found, if the vibrational modes of the host lattice are known, by mathematical techniques which we discuss later. The dynamics of the host lattice are not, of course, known from first principles, but they can be calculated parametrically from the observed properties of the crystal on the basis of a model. Such a model discusses the forces in the crystal, not in the terms used above, but in terms of a Taylor expansion of the potential in powers of the displacement of the atoms. The coefficients are taken to be parameters and are harmonic or anharmonic (see Section I.2), and central or noncentral according as the potential they describe does not or does depend on the direction of the bond.

The parameters of this model have already been evaluated for the perfect forms of the crystals this thesis will be concerned with, and we deal only with the theory of defects. This theory is considerably older than the experimental work (which commenced with Schaefer's observation of a localized mode due to H^- in KCl in 1960), dating from work by Rayleigh in 1877. His theorem states that in a vibrating system a perturbation which has the form of a mass increase in one of the particles or a force constant decrease, will cause all the eigenfrequencies to decrease in such a way that the levels always lie in the gap between an unperturbed level and its neighbour. The converse effect is produced by decreasing one of the masses or increasing a force constant. In the latter case, the highest eigenfrequency may lift out of the band of

unperturbed frequencies, creating the localized mode first observed by Schaefer. A review of the theory is given by Maradudin, Montroll & Weiss (1963).

We are here concerned with two ways in which a defect may tell us something about the forces in an insulating crystal. The first involves a study of the polarizability of the atoms, an effect of particular importance in non-ionic crystals. To do this we make use of the fact that a charged defect will polarize the atoms in the host lattice, and we study the absorption of light by the vibrations of these polarized host atoms. The second approach makes use of the large amplitude of vibration of a very light defect. This large amplitude makes anharmonic effects important, and so we can learn something about these higher terms in the potential more directly than by studies of thermal expansion and conductivity.

I.2. Shell Model in Perfect Lattices

The simplest view that can be taken of the forces coupling atoms in a perfect crystal is that they are represented by springs following Hooke's law. This view can be dervied from a Taylor expansion, in powers of atomic displacements, $U\binom{\ell}{K}$, of the potential, ϕ, describing the forces on an atom at site K of unit cell ℓ.

$$\phi = \phi_0 + \sum_{\ell K \alpha} \phi_\alpha \binom{\ell}{K} u_\alpha \binom{\ell}{K} + \frac{1}{2} \sum_{\substack{\ell K \alpha \\ \ell' K' \beta}} \phi_{\alpha\beta} \binom{\ell \ell'}{K K'} u_\alpha \binom{\ell}{K} u_\beta \binom{\ell'}{K'} + \cdots$$

For equilibrium in the static case, the terms linear in $u\binom{\ell}{K}$ vanish, and if we neglect terms of order higher than the second, we are left with Hooke's law forces, otherwise known as the harmonic approximation.

Since an evaluation of $\Phi_{\alpha\beta}\binom{\ell\ \ell'}{K\ K'}$ from first principles is not yet possible, and its elements are consequently treated as parameters to be found, it is important to restrict the number of independent elements as much as possible. The dependence of $\Phi_{\alpha\beta}\binom{\ell\ \ell'}{K\ K'}$ on its subscripts is to a great extent determined by the symmetry of the system, which in a perfect crystal consists of both point and translational symmetries. Thus we have that $\Phi_{\alpha\beta}\binom{\ell\ \ell'}{K\ K'} = \Phi_{\alpha\beta}\binom{\ell-\ell'}{K\ K'}$ from the latter, so that the matrix describing Φ is a circulant; and that

$$\Phi_{S\alpha S\beta}\binom{\ell\ S\ell'}{K\ SK'} = \Phi_{\alpha\beta}\binom{\ell\ \ell'}{K\ K'}$$

as a result of the former, where S describes any operation of the point group about site (ℓ, K). If nonprimitive translations are involved, this notation must be generalized. Furthermore, since the internal forces are independent of rigid displacement of the crystal, and since the form of the forces is independent of homogeneous deformation, general conditions may be imposed upon $\Phi_{\alpha\beta}\binom{\ell\ \ell'}{K\ K'}$:

$$\sum_{\ell' K'} \Phi_{\alpha\beta}\binom{\ell\ \ell'}{K\ K'} = 0$$

$$\sum_{\ell' K' \alpha} \Phi_{\alpha\beta}\binom{0\ \ell'}{K\ K'} R_\lambda\binom{\ell'\ 0}{K'\ K} = 0$$

where $\underline{R}\binom{l'}{\kappa'}{0}{\kappa} = \underline{R}\binom{l'}{\kappa'} - \underline{R}\binom{0}{\kappa}$, the relative position of sites (l',κ') and $(0,\kappa)$, (Maradudin, Montroll & Weiss, 1963).

However, to deal adequately with most crystals even in the harmonic approximation, the Hooke's law spring model above must be elaborated. The first consideration is that, even with symmetry restrictions the number of independent parameters to be found becomes rapidly very large as the range of the interaction is increased, unless we assume some particular dependence of the force on distance from the originating displacement. What is commonly done is to divide the forces into two parts; a general part, restricted only by symmetry considerations (or sometimes by a requirement that forces be central), extending to a few close neighbours; and a long-range part based on the Coulomb interaction of electric dipoles created by the displacement of charged ions. This part is

$$\Phi^{c}_{\alpha\beta}\binom{l\,l'}{\kappa\kappa'} = -Z_\kappa Z_{\kappa'} \left[\frac{\partial^2}{\partial u_\alpha\binom{l}{\kappa}\partial u_\beta\binom{l'}{\kappa'}} \; \frac{1}{|\underline{R}_{\alpha\beta}\binom{l-l'}{\kappa\kappa'} + \underline{x}|} \right]_{x=0}$$

where $\underline{x} = \underline{u}\binom{l}{\kappa} - \underline{u}\binom{l'}{\kappa'}$, and Z_κ is the (effective) charge on the ion. We need to consider the Fourier transform,

$$D^{c}_{\alpha\beta}\binom{q}{\kappa\kappa'} = -Z_\kappa Z_{\kappa'} \sum_{l} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \; \frac{e^{-i\underline{q}\cdot\underline{R}\binom{l\,0}{\kappa\kappa'}}}{|\underline{r}\binom{l}{\kappa\kappa'} + \underline{x}|}$$

in which the sum converges only slowly, and the limit is not well defined at $\underline{q}=0$. These difficulties were resolved by Ewald (1917) and by Huang (1949). Ewald split the sum into two rapidly converging sums, one over real space and one over $\underline{q}$-space. Huang showed that this permits one to isolate the part with an undefined limit at $\underline{q}=0$ which is thought of as a macroscopic electric field depending on the shape of the specimen. Kellerman (1940) used Ewald's method to calculate $\frac{D_{\alpha\beta}(\underline{q}_{KK'})}{Z_K Z_{K'}}$ which are known as the Kellerman coefficients. A set of Kellerman coefficient for calcium fluoride structure (and any structure which is a subset of this) were made available for this work on magnetic tape by Dr. C.T. Sennett at the Royal Radar Establishment, Great Malvern, where computing facilities were kindly extended to us.

A second elaboration must be made on this model of rigid ions interacting by harmonic short-range and Coulomb forces, and yields a model which is conceptually, although not formally, a generalization, called the Shell Model. (see e.g. Cochran, 1959; Dolling & Waugh, 1963). The Shell model conceives of each atom in the lattice as polarizable, by separating from the nucleus (which carries most of the mass) a spherical shell of electrons, connected to it by a central force. Formally, this has the effect of doubling the number of equations describing each unit cell. The adiabatic appoximation is usually incorporated by supposing that the electron shell is in fact massless. Thus, where A, B, C are $3N \times 3N$ matrices in real space describing

interactions between, respectively, core and core, core and shell, and shell and shell; and $\mathcal{C}$ gives Kellerman coefficients in real space

$$M\omega^2 \xi_\alpha\binom{\ell}{K} = \sum_{\ell' K' \beta} \left\{ A_{\alpha\beta}\binom{\ell\ell'}{KK'} + X_K \mathcal{C}_{\alpha\beta}\binom{\ell\ell'}{KK'} X_{K'} \right\} \xi_\beta\binom{\ell'}{K'} + \left\{ B_{\alpha\beta}\binom{\ell\ell'}{KK'} + X_K \mathcal{C}_{\alpha\beta}\binom{\ell\ell'}{KK'} Y_{K'} \right\} \eta_\beta\binom{\ell'}{K'}$$

$$m\omega^2 \eta_\alpha\binom{\ell}{K} = \sum_{\ell' K' \beta} \left\{ B^\dagger_{\alpha\beta}\binom{\ell\ell'}{KK'} + Y_K \mathcal{C}_{\alpha\beta}\binom{\ell\ell'}{KK'} X_{K'} \right\} \xi_\beta\binom{\ell'}{K'} + \left\{ C_{\alpha\beta}\binom{\ell\ell'}{KK'} + Y_K \mathcal{C}_{\alpha\beta}\binom{\ell\ell'}{KK'} Y_{K'} \right\} \eta_\beta\binom{\ell'}{K'}$$

where $\underline{\xi}\binom{\ell}{K}$ is the displacement of the $(\ell,K)^{th}$ core, which has a charge X_K and mass M, and $\underline{\eta}\binom{\ell}{K}$ is the displacement of the $(\ell,K)^{th}$ shell, with charge Y_K and mass m.

Because we shall be using the Shell model for crystals of neutral atoms, $X_K = -Y_K$, it is useful to change to centre-of-mass coordinates $\underline{u} = (M\underline{\xi} + m\underline{\eta})/(M+m)$, $\underline{w} = \underline{\xi} - \underline{\eta}$. In this case, the condition of invariance of the forces under translation of the system gives

$$\sum_{\ell' K'} A_{\alpha\beta}\binom{\ell\ell'}{KK'} + B_{\alpha\beta}\binom{\ell\ell'}{KK'} = 0$$

$$\sum_{\ell' K'} B^\dagger_{\alpha\beta}\binom{\ell\ell'}{KK'} + C_{\alpha\beta}\binom{\ell\ell'}{KK'} = 0$$

Making the coordinate transformation, we have, formally,

$$\begin{pmatrix} R - M\omega^2 & S \\ S^\dagger & T + Y\mathcal{C}Y \end{pmatrix} \begin{pmatrix} u \\ w \end{pmatrix} = 0$$

where

$$R \equiv A + 2B + C$$

$$S \equiv B + C$$

$$T \equiv C$$

and we have made the adiabatic approximation that $m=0$. The conditions for translational invariance of forces give

$$\sum_{\kappa'\kappa'} A_{\alpha\beta}\begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} = 0$$

$$\sum_{\ell'\kappa'} S_{\alpha\beta}\begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} = 0 \qquad (1)$$

which means that these two matrices behave like ϕ in the simpler model.

Before we discuss the solutions for the Shell model, there is a further extension to the formalism, due to Page & Strauch (1968), whose use will become apparent when we consider the problem of defects with altered charges. This involves writing out explicitly the long-range Coulomb contribution, as follows:

$$\begin{pmatrix} R-M\omega^2 & S & Z \\ S^\dagger & T & Y \\ Z & Y & -e^{-1} \end{pmatrix}\begin{pmatrix} u \\ w \\ E \end{pmatrix} = 0 \qquad (2)$$

where Z is the charge of the whole ion, $Z = X+Y$ (we have considered the general case again), and the new vector, $E = e(Zu+Yw)$, is the electric field generated at one site by the dipole moments $Zu+Yw$ through the rest of the crystal. In this formal notation, Z, X, Y have the form of diagonal matrices of equal diagonal blocks the size of the unit cell.

In the phonon problem, we are interested in the displacements u ,

rather than in the electronic excitations w or the field E. To solve the model, therefore, we eliminate E and w and obtain for u the usual Shell model result

$$M\omega^2 u = [R - S(T+Y\mathcal{C}Y)^{-1}S^{\dagger}]\,u \qquad (3)$$

This is an eigenvalue equation which can be solved by the usual techniques of phonon theory, since it is formally equivalent to the result of the simplest model

$$M_K\omega^2 u_\alpha\binom{l}{K} = \sum_{l'K'\beta} \Phi_{\alpha\beta}\binom{l\,l'}{K\,K'} u_\beta\binom{l'}{K'} \qquad (4)$$

In the perfect lattice, this solution is obtained by Fourier transforming the equation, since the matrices are circulants and, by applying the theory of Abelian groups, can be shown to be diagonalized in this way. The resulting equation involves a matrix which is only the size of the unit cell

$$M_K\omega^2 u_\alpha(K) = \sum_{K'\beta} D_{\alpha\beta}\left(\frac{q}{K\,K'}\right) u_\beta(K')$$

where

$$u_\alpha\binom{l}{K} = u_{\alpha(K)}\, e^{i\underline{q}\cdot\underline{R}\binom{l}{K}}$$

and the "dynamical matrix"

$$D_{\alpha\beta}\left(\frac{q}{K\,K'}\right) = \sum_{l} \Phi_{\alpha\beta}\binom{l\;0}{K\;K'}\, e^{-i\underline{q}\cdot\underline{R}\binom{l\;0}{K\;K'}}.$$

$\underline{R}\binom{l\;0}{K\;K'} = \underline{R}\binom{l}{K} - \underline{R}\binom{0}{K'}$ has been defined above as the relative equilibrium position of sites (l,K) and $(0,K')$.

Since Fourier transforming block-diagonalizes translationally symmetric matrices in this way, the form of (3) remains unchanged, and so we distinguish the matrices in real space from their forms in $\underline{q}$-space by the notation of the subscripts, e.g.

$$R_{\alpha\beta}\begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix}$$

and

$$R_{\alpha\beta}\begin{pmatrix} \underline{q} \\ \kappa\kappa' \end{pmatrix} = \sum_{\ell} R_{\alpha\beta}\begin{pmatrix} \ell & 0 \\ \kappa & \kappa' \end{pmatrix} e^{-i\underline{q}\cdot\underline{R}\begin{pmatrix} \ell & 0 \\ \kappa & \kappa' \end{pmatrix}}.$$

In $\underline{q}$-space, then, (3) is a $3r \times 3r$ equation, where r is the number of values of κ, i.e. the number of atoms in the unit cell.

Because of the conditions (1), $R(\underline{q}=0)$ and $S(\underline{q}=0)$ are singular and some of the $3r$ eigenvalues, $\omega_j^2(\underline{q})$, of (3) vanish at $\underline{q}=0$. This number is 3 (see, e.g. Maradudin, Montroll & Weiss, 1963), and these solutions, called the acoustic modes, correspond to the long-wavelength vibrations of an eleastic continuum. The motion involves a displacement of the whole unit cell. The remaining $3(r-1)$ solutions have a finite frequency at $\underline{q}=0$, and are called the optic modes, since the motion is within the unit cell, leaving its centre of mass unchanged. In ionic crystals this can create vibrating electric dipoles, which can interact with light of suitable frequency and wave vector.

The polarization, $Y w$, of an atom is given by (2) in terms of u

$$Yw = -Y(T+Y\epsilon Y)^{-1}S^{\dagger}u.$$

The exciton motion, w', can be obtained if we subtract $m\omega^2$ from T in (2) and solve, noting that the motion has too high a frequency to be followed by the cores, so that $u=0$:

$$m\omega^2 w = (T+2\epsilon Y)w$$

This eigenvalue equation has properties similar to the proceeding one, and can be diagonalized by Fourier transformation. The solution of the resulting dynamical equation gives $3r$ eigenvalues for each value of q. These differ from the phonon modes notably in that (1) does not apply to $T+2\epsilon Y$, which is not singular at $q=0$. Thus the exciton modes remain at high frequencies, and do not come to zero at zero wave vector.

I.3 Perfect Lattice Green's Function

The substitution of an atom of different mass and chemical properties for one of the atoms of the host lattice removes the translational symmetry of the crystal, and (3) can no longer be diagonalized by Fourier transformation if its component matrices refer to an imperfect lattice. However, if we know the results for the perfect lattice, the imperfect lattice may be solved in principle as follows, and in practice if we assume that the defect is limited in extent (that is, if its direct interactions with the host lattice, through changed force constants or other, extend only for a few neighbours).

In our treatment, we consider the simplest model, since the extension to the Page & Strauch version of the Shell model is a trivial

addition of subscripts. Then (4) becomes

$$M\omega^2 u_\alpha\begin{pmatrix}\ell\\ \kappa\end{pmatrix} - \sum_{\ell'\kappa'\beta} \Phi_{\alpha\beta}\begin{pmatrix}\ell\ell'\\ \kappa\kappa'\end{pmatrix} u_\beta\begin{pmatrix}\ell'\\ \kappa'\end{pmatrix} = \sum_{\ell'\kappa'\beta} C_{\alpha\beta}\begin{pmatrix}\ell\ell'\\ \kappa\kappa'\end{pmatrix} u_\beta\begin{pmatrix}\ell'\\ \kappa'\end{pmatrix}$$

where quantities on the left-hand side refer to the perfect lattice and

$$C_{\alpha\beta}\begin{pmatrix}\ell\ell'\\ \kappa\kappa'\end{pmatrix} = -\delta_{\alpha\beta}\delta_{\ell\ell'}\delta_{\ell_0}\delta_{\kappa\kappa'}\delta_{\kappa_1}\Delta M_{\kappa_1}\omega^2 + \Phi_{\alpha\beta}\begin{pmatrix}\ell\ell'\\ \kappa\kappa'\end{pmatrix}$$

where ΔM is the change in mass at the defect and Φ the change in force constants. This can be written formally

$$(M\omega^2 - \Phi)\, u = C\, u$$

or, as an eigenvalue equation

$$u = g(\omega^2)\, C\, u \tag{5}$$

where

$$g(\omega^2) = (M\omega^2 - \Phi)^{-1} \tag{6}$$

the perfect lattice Green's function.

Since the quantities in (6) refer to the perfect lattice, the matrix inversion can be performed after diagonalizing Φ as in the pprevious section, and the final result obtained by performing the inverse Fourier transformation on the inverted diagonal blocks. If the defect is limited in extent, C is a matrix consisting of zeroes everywhere but in the small square block describing the region around the defect. This region may be labelled Δ , and if we are concerned

only to find the values of u in this region, we have instead of (5)

$$u_\Delta = g_{\Delta\Delta}(\omega^2)\, C_{\Delta\Delta}\, u_\Delta \qquad (5')$$

which involves finding $g(\omega^2)$ only over a small region. This is an important consideration because $g(\omega^2)$ must be found by computer, since the second Fourier transform requires a sum to be made over a large number of $\underline{q}$-values, some of the 10^{23} modes in which the lattice can vibrate. Furthermore, (6) cannot be computed as it stands, for the perfect lattice solutions, at the zeros of $M\omega^2-\Phi$, correspond to poles in $g(\omega^2)$. To avoid difficulties, we add a small imaginary part, ϵ, to ω^2. Since, when (6) is diagonalised,

$$g(\omega^2) = \sum_{\underline{q}j} \frac{1}{\omega^2-\omega_j^2(\underline{q})}$$

and

$$\lim_{\epsilon\to 0} \frac{1}{x+i\epsilon} = P\left(\frac{1}{x}\right) - i\pi\,\delta(x),$$

the poles in (6) are replaced by imaginary delta-functions, or by an approximation to a delta-function since ϵ is not taken to the limit zero.

With these considerations we convert (6) to a computable form,

$$g^{ij}_{\alpha\beta}\left(\begin{smallmatrix}l_0\\ \kappa\kappa'\end{smallmatrix}, \omega^2+i\epsilon\right) = \frac{1}{N}\sum_{\underline{q}} e^{i\underline{q}\cdot\underline{R}\left(\begin{smallmatrix}l_0\\ \kappa\kappa'\end{smallmatrix}\right)} \Delta^{-1\,ij}_{\alpha\beta}\left(\begin{smallmatrix}\underline{q},\\ \kappa\kappa'\end{smallmatrix}, \omega^2+i\epsilon\right) \qquad (7)$$

where

$$\Delta^{ij}_{\alpha\beta}\left(\begin{smallmatrix}\underline{q},\\ \kappa\kappa'\end{smallmatrix}, \omega^2+i\epsilon\right) = M_\kappa \delta_{\kappa\kappa'}\delta_{\alpha\beta}\delta_{ij}\delta_{jl}(\omega^2+i\epsilon) - D^{ij}_{\alpha\beta}\left(\begin{smallmatrix}\underline{q}\\ \kappa\kappa'\end{smallmatrix}\right)$$

and we have now included the indices $i,j = 1,2,3$ referring to the components of the Page & Strauch version of the Shell model given by (2). We do the sum over $\underline{\ell}$ in two stages, first over the star of $\underline{\ell}$, that is over all $\underline{\ell}$ of common magnitude, then over all different $|\underline{\ell}|$. If S is the transformation from an initial $\underline{\ell}$ to $S\underline{\ell}$ in the star of $\underline{q}$, we can make use of the result (see e.g. Melvin Lax's unpublished book on group theory in crystals)

$$D^{ij}\begin{pmatrix} S\underline{\ell} & \\ & \end{pmatrix} = \sum_{\ell} \Phi^{ij}\begin{pmatrix} \kappa & 0 \\ \kappa\kappa' & \end{pmatrix} e^{-iS\underline{\ell}\cdot\underline{B}\begin{pmatrix} \ell & 0 \\ \kappa\kappa' & \end{pmatrix}}$$

$$= \sum_{\ell} S\cdot\Phi^{ij}\begin{pmatrix} S^{-1}\ell & 0 \\ S^{-1}\kappa & S^{-1}\kappa' \end{pmatrix}\cdot S^{-1} e^{-i\underline{q}\cdot\underline{B}\begin{pmatrix} S^{-1}\kappa & 0 \\ S^{-1}\kappa & S^{-1}\kappa' \end{pmatrix}}$$

$$= S\cdot D^{ij}\begin{pmatrix} \underline{q} & \\ S^{-1}\kappa, & S^{-1}\kappa' \end{pmatrix}\cdot S^{-1}$$

which therefore applies to Δ and to Δ^{-1}. (The dependence of the above on the Cartesian indices α,β is implicit in the matrix notation.) The sum in (7) is over S, which in a cubic system is any of the 48 rotations of the group O_h. We reduce it to a sum over the 24 members of T_d by adding to the summand in the identical term in $S(-\underline{q})$. This is helpful because in Si and CaF_2, the systems of interest, T_d leaves the sublattices invariant. The final appearance of (7) depends on which of the two systems to be treated in this thesis we are concerned with.

Since

$$D^{\dagger}(\underline{q}) = D^{*}(\underline{q}) = D(-\underline{q})$$

we have

$$\Delta^{T}_{\alpha\beta}(\underline{q},\omega^2+i\epsilon) = \Delta^{*}_{\alpha\beta}(\underline{q},\omega^2-i\epsilon) = \Delta_{\alpha\beta}(-\underline{q},\omega^2+i\epsilon)$$

and

$$\Delta^{-1\,T}_{\beta\alpha}(\underline{q},\omega^2+i\epsilon) = \Delta^{-1\,*}_{\alpha\beta}(\underline{q},\omega^2-i\epsilon) = \Delta^{-1}_{\alpha\beta}(\underline{q},\omega^2+i\epsilon)$$

From these relations, we obtain for (7) in the case of diamond structure

$$g^{ij}_{\alpha\beta}\begin{pmatrix}0&0\\K&K\end{pmatrix}\omega^2+i\epsilon) = \sum_{|\underline{q}|}\sum_{S\in T_d} S_{\alpha\alpha'}\,\Delta^{-1\,ij}_{\alpha'\beta'}\begin{pmatrix}\underline{q}\\K&K\end{pmatrix}\omega^2+i\epsilon)\,S^{-1}_{\beta'\beta} + \text{transpose} \quad (8)$$

where in this case we are only concerned with the Green's function at the defect site $(0,K)$ itself. For CaF_2, we shall need the Green's function at various sites near the defect, but only at $\omega=0$. Hence it is possible to put $\epsilon=0$, since the only singularity will occur at $\underline{q}=0$, and this $\underline{q}$-value can be avoided and accounted for by other means. Thus we can use the relation between $\Delta(-\underline{q})$ and $\Delta^{*}(\underline{q})$ above, which is much more convenient, as we need only compute the real part of the Green's function:

$$g^{11}_{\alpha\beta}\begin{pmatrix}\ell&0\\K&K'\end{pmatrix}0) = \frac{1}{N}\sum_{|\underline{q}|}\sum_{S\in T_d} e^{i\underline{S}\underline{q}\cdot\underline{R}\begin{pmatrix}\ell&0\\K&K'\end{pmatrix}} S_{\alpha\alpha'}\,\Delta^{-1\,11}_{\alpha'\beta'}\begin{pmatrix}\underline{q}\\K&K'\end{pmatrix}0)\,S^{-1}_{\beta'\beta} + \text{c.c.}$$

$$= -\frac{1}{N}\sum_{|\underline{q}|}\sum_{S\in T_d} e^{i\underline{S}\underline{q}\cdot\underline{R}\begin{pmatrix}\ell&0\\K&K'\end{pmatrix}} S_{\alpha\alpha'}\,D^{-1\,11}_{\alpha'\beta'}\begin{pmatrix}\underline{q}\\K&K'\end{pmatrix}\,S^{-1}_{\beta'\beta} + \text{c.c.} \quad (9)$$

In CaF_2, we do not use the Shell model, which is equivalent to $\alpha=1$. It is important to note here that $D(\underline{q})$ is Hermitian, and that the

inversion symmetry of CaF_2 enables it to be transformed to a real symmetric matrix, which greatly simplifies the computational labour of finding its inverse. In the expressions above, the Einstein summation convention is used for the Cartesian indices.

In point of fact, we do not use (5) or (5') in either of the problems which follow in this thesis, but we require both $g(\omega^2)$ and C. Appendix I will give a more detailed discussion of the computation of $g(\omega^2)$. In the next section we consider the form of C for silicon, and the advantages of the Page & Strauch formulation of the Shell model.

1.4 The Shell Model in the Imperfect Lattice

Page & Strauch write their Shell model equations in the form (2) in order to write the Coulomb forces explicitly. This enables us to change the charge on the defect, as well as its mass and force constants, and to incorporate in the calculations the changes in the dipole-dipole coupling of the vibrating defect with the rest of the lattice. Thus, for example, in (5), Φ in C becomes

$$\Phi = \begin{pmatrix} \Delta R & \Delta S & \Delta Z \\ \Delta S^T & \Delta T & \Delta Y \\ \Delta Z & \Delta Y & -\Delta(\quad) \end{pmatrix} \qquad (10)$$

where the condition of invariance of forces under uniform translation gives

$$\Delta R = -\Delta Z \otimes \Delta Z$$

$$\Delta S = -(X+\Delta X) \otimes \Delta Z$$

which vanish if we consider changes only on the defect itself. The

change in the polarizability at the defect can be given either by $\Delta\Gamma$ or by ΔY.

The change in the Kellerman coefficients, given by $-\Delta\mathcal{C}^{-1}$, requires some attention. In a perfect crystal, the diagonal terms in the long range part of the potential, ϕ^c, vanish. They are given by the condition of invariance of forces under translation of the whole crystal (Born & Huang, section 27)

$$\phi^c_{\alpha\beta}\begin{pmatrix}0\\ \kappa\kappa'\end{pmatrix} = -Z_\kappa \sum{}' Z_{\kappa'} \left\{ \frac{\partial^2}{\partial R_\alpha \partial R_\beta} \frac{1}{|R|} \right\}_{\underline{R}=\underline{R}\begin{pmatrix}l\\ \kappa\kappa'\end{pmatrix}}$$

which is a function of odd powers of R. The prime on the summation excludes the term $\begin{pmatrix}l\\ \kappa'\end{pmatrix} = \begin{pmatrix}0\\ \kappa\end{pmatrix}$, since we are only interested in what is called the "exciting field." Because of the symmetry about the origin of each shell of similarly charged neighbours, however, the rest of this sum vanishes in the perfect crystal. In a crystal in which one of the sites has a charge change, ΔZ, the symmetry is broken, and the diagonal part of ϕ^c is now zero nowhere except at the defect site itself. This requires us to specify the diagonal terms in the imperfect crystal, and we write them symbolically as $\Delta\mathcal{C}$, which falls off as $1/R^3$ with distance from the defect.

If we were discussing a change in shell charge, ΔY, in the Shell model, the above does not apply, for the change in core charge on the same atom exactly counterbalances the effect.

These consideration indicate that the method of Page & Strauch cannot directly be used in ionic crystals such as CaF_2 to accommodate changed defect charges. In a homopolar crystal such as Silicon, of course, the digonal terms of Φ^c , above, vanish (unless there is more than one charge defect present), and the method may be used. Considering (5), $g(\omega^2)$ may be written more fully

$$\begin{pmatrix} g^{11} & g^{12} & g^{13} \\ g^{21} & g^{22} & g^{23} \\ g^{31} & g^{32} & g^{33} \end{pmatrix}$$

where the defining equation for $g(\omega^2)$

$$g(\omega^2)(M\omega^2 - \Phi) = I$$

gives

$$\begin{aligned}
g^{11} &= [R - M\omega^2 - S T_c^{-1} S^\dagger]^{-1} \\
g^{12} &= -g^{11} S T_c^{-1} = -A^{-1} S g^{22} \\
g^{21} &= -g^{22} S^\dagger A^{-1} = -T_c^{-1} S^\dagger g^{11} \\
g^{22} &= [T_c - S^\dagger A^{-1} S]^{-1} \\
g^{33} &= (g^{31} Z + g^{32} Y - I) C = C(Z g^{13} + Y g^{23} - I) \\
g^{13} &= (g^{11} Z + g^{12} Y) C \\
g^{31} &= C(Z g^{11} + Y g^{21}) \\
g^{23} &= (g^{21} Z + g^{22} Y) C \\
g^{32} &= C(Z g^{12} + Y g^{22})
\end{aligned} \qquad (11)$$

where

$$T_c = T + Y \in Y$$
$$S_c = S + Z \in Y = S$$
$$R_c = R + Z \in Z = R$$

and $$A = R - M\omega^2.$$

We note that $g^{(j)}, (j = 1,2$, are exactly the Green's functions of the usual Shell model.

The relations (11) hold for $\Delta^{-1}(\omega)$ as well as for $g^{(j)}$, and were used in the evaluation of (8). They hold for perfect and imperfect lattices.

CHAPTER II

One-Phonon Optical Absorption by Lattice Vibrations

II.1.

The chief mechanism whereby light interacts with matter is through an oscillating electric dipole or charge. In perfect ionic crystals, light can be absorbed by creating a single optical phonon, for the reason discussed in Section I.1. The translational symmetry of the perfect crystal imposes the selection rule that the total wavevector of photon and phonon must be conserved. This rule and that of energy conservation are satisfied together only at one frequency, the Reststrahl frenquency, which is very near the $q = 0$ transverse optical mode frequency. Thus the one-phonon absorption spectrum of a perfect ionic crystal is essentially a delta-function at the Reststrahl frequency. A perfect homopolar crystal, containing neutral atoms, does not show any absorption. Even when the Shell model is used and shell and core charges are assumed for each atom, it is shown by Cochran (1959) that this result is obtained.

The introduction of an impurity into the crystal has two effects. It destroys the translational symmetry and hence the selection rule that an ionic crystal is permitted only Reststrahl absorption. Secondly, if it is charged, it absorbs light in its own oscillations.

The symmetry of an imperfect crystal is only that of the point group about the defect, and so those modes which can interact with light through one phonon processes are much greater in number. The absorption, instead of being a delta-function at the Reststrahl frequency is now proportional to the density of states of these optically active modes. This must be calculated for the imperfect crystal. The imperfect crystal density of states is qualitatively similar to that of the perfect crystal except in the region of the frequency at which the defect vibrates.

The defect modes can be of two types, localized modes or resonances (we do not consider separately gap modes, which resemble localized modes). If the defect is lighter than the host atoms (ions), or if it is coupled to the lattice by forces stronger than those found in the rest of the lattice it will vibrate at a frequency higher than the maximum frequency of the host lattice band, as discussed in Chapter I. (Often a lighter defect is coupled to the lattice by weakened force constants, leading to such a case, but with a somewhat lower frequency than would be given by th mass change alone). In this case, the host lattice is unable to transmit the vibrational energy of the defect, which remains localized on and near the defect itself. This localized mode appears in the density of states (and in the absorption if it is active) as a Lorentzian peak isolated from the band modes and at a higher frequency. The resonant mode, on the other hand, is caused by a defect vibrating at a frequency within the band The lattice is in this case able to transmit the vibration energy away

from the defect, and so the mode is not strictly localized in real space. Its behaviour, indeed, resembles a resonance in a scattering problem, and it can be thought of as an unstable state, decaying rapidly away into the modes of the host lattice. It thus has a fairly large energy width, although it is recognizable as a hump on the perfect lattice density of states and absorption, if it is not in a position to be disguised behind the usual acoustic or optic mode peaks in the density of states. These are the major features of the vibrations of a lattice containing a defect.

In the case of polarizable atoms or ions in a crystal, both perfect and imperfect lattice absorption are modified by the Lorentz correction factor. This factor can be derived from the Shell model, as we shall show, and amounts to an enhancement of the electric field of the light as seen by the dipoles in the crystal, owing to the polarization of the atoms by that field. The field seen within the crystal is

$$E_{loc} = E + 4\pi P/3 = \left(1 + \frac{4\pi}{3}\chi\right)E$$

where χ is the susceptibility of the crystal. We shall show that this factor is contained in the Shell model formalism.

If the defect is charged, it absorbs light itself, and this case has been discussed by Dawber & Elliott (1963 a, b) for both localized and resonant modes of defects in silicon. More recently, Leigh

and Szigeti (1967) have discussed a second absorption mechanism which will operate in a polarizable lattice containing a charged defect. This gives rise to an absorption by the band modes, owing to the "apparent charges" induced on the host atoms by the charge. These are related to the displacement-dependent parts of the host atom polarizabilities, which give rise to Raman scattering and related effects. Thus a charged defect, even when stationary, can cause improved absorption in a polarizable crystal. The polarizing field, following the Coulomb law, is long range in its effect, and so this type of defect is not accessible to the methods described in the last chapter, and must be treated specially.

II.2. Optical Absorption

We first consider the general form of optical absorption in terms of the Green's functions of Chapter I. The transmitted light intensity, I, varies exponentially with the thickness, r, of the sample, and is given by Lambert's law

$$I = I_0 e^{-K(\omega) r}$$

where $K(\omega)$ is the frequency-dependent absorption coefficient. This form is to be compared with the electric field of an electromagnetic wave

$$\underline{E} = \underline{E}_0 e^{i(\omega t \pm n\underline{k}\cdot\underline{r})}$$

where ω is the angular frequency, $\underline{k}$ is the wavevector of the light in vacuo, of magnitude

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{c}$$

and n is the index of refraction of the crystal. Since the susceptibility, χ, dielectric constant, κ, and refractive index n are related by (in the case of unit magnetic permeability)

$$n^2 = \kappa = 1 + 4\pi\chi ,$$

we have, on taking the squared modulus of $\underline{E}$,

$$\kappa(\omega) = \frac{4\pi\omega\chi^{(2)}}{c n^{(1)}} \qquad (1)$$

where the superscripts (1) and (2) refer to the real and imaginary parts, respectively, and where the susceptibility, χ, is in general a function of ω.

It is easy to show, by extending the considerations of Chapter I, that the susceptibility is simply related to the Green's function of the system, perfect or imperfect. The displacements, u_i, of ions (or shells) are given by (I.5) where Cu can be written F, the applied force:

$$\underline{u}_i = \sum_j g_{ij} \underline{F}_j = \sum_j g_{ij} Z_j e \underline{E} , \qquad (2)$$

and the resulting dipoles are

$$Z_i e \underline{u}_i = e^2 \sum_j Z_i g_{ij} Z_j \underline{E} ,$$

This gives the dipole moment per unit volume, $\underline{P}$, and hence the susceptibility, which is the proportionality factor relating $\underline{P}$ and

the applied electric field $\underline{E}$:

$$\chi = \frac{e^2}{V} \sum_{ij} Z_i g_{ij} Z_j \qquad (3)$$

The electronic charge is $-e$, V is the volume of the crystal, and the sum is over all sites carrying charge Ze .

If the lattice is imperfect, the same formal notation goes through, except that it is customary to write G , the imperfect lattice Green's function, in place of g for the perfect lattice. The two are related by the Dyson equation

$$G = g + gCG \qquad (4)$$

which can be put in the form

$$G = \frac{1}{1-gC}\, g \qquad (5)$$

where C is the difference between matrices describing imperfect and perfect lattices. This enables us to extend the qualitative discussion at the beginning of this chapter of the relation between absorption by imperfect and perfect lattices. We require the imaginary part of G ,

$$G^{(2)} = \frac{g^{(2)}}{(1-g^{(1)}C)^2 + (g^{(2)}C)^2}$$

which clearly responds to all frequencies of light absorbed by the perfect lattice, owing to the numerator. The denominator creates a

resonance at $1 = g^{(1)}C$, when this occurs within the range for which $g^{(2)}$ is not zero. For example, in the case of a defect with mass change only in a simple rigid-ion model, $C = M\epsilon\omega^2$ where $\epsilon = (M-M')/M$, and resonances occur in the band, $\omega < \omega_{MAX}$, for $M' > M$. The term in $g^{(2)}$ gives a finite width to this resonance in the band.

Outside the band, $g^{(2)} = 0$, and hence $G^{(2)} = 0$, unless we add a small imaginary part, $-i\epsilon$, to the frequency. Then we can Taylor-expand the denominator of

$$G = \frac{g^{(1)}(\omega)}{1 - g(\omega)C} \equiv \frac{g^{(1)}(\omega)}{f(\omega)} \simeq \frac{g^{(1)}(\omega)}{(\omega - i\epsilon - \omega_L) f'(\omega_L)}$$

about the point, ω_L , where it vanishes. Taking the limit $\epsilon \to 0$ we have

$$\mathrm{Im}\, G = \pi \frac{g^{(1)}(\omega)}{f'(\omega)} \delta(\omega - \omega_L)$$

giving a delta-function absorption at the localized mode energy, ω_L . A more useful quantity to obtain is the integrated intensity of this absorption, which is proportional to

$$\int d\omega\, \mathrm{Im}\, G = \pi \frac{g^{(1)}(\omega_L)}{f'(\omega_L)} \,. \qquad (6)$$

II.3. Optical Absorption in the Shell Model

We now write (3) in greater detail , in terms of the Shell model, so that some of the mechanisms of Section II.1 can be incorporated into the absorption. We shall soon specialize our considerations to homopolar crystals such as silicon. The equation can be written for the imperfect crystal

$$\chi = \frac{e^2}{V} \sum_{\substack{\ell\kappa\alpha i \\ \ell'\kappa'\beta j}} Z^i\begin{pmatrix}\ell\\ \kappa\end{pmatrix} G^{ij}_{\alpha\beta}\begin{pmatrix}\ell\ell'\\ \kappa\kappa'\end{pmatrix} Z^j\begin{pmatrix}\ell'\\ \kappa'\end{pmatrix}$$

which has the same meaning in the ordinary Shell model (i,j = 1, 2) as in the Page & Strauch version (i, j = 1, 2, 3) if Z^1 = ionic charge, Z^2 = shell charge, $Z^3 = 0$. Since the vector Z^i is just $(\phi - \phi^{33})^{3i}$ (see (I.2)), we have

$$\chi \propto \sum\left[(\phi-\phi^{33})G(\phi-\phi^{33})\right]^{33} = \sum\left(-\phi^{33} + \phi^{33}G^{33}\phi\right)$$

$$= \epsilon^{-1}_{(\underline{q}=0)} + \epsilon^{-1}_{(\underline{q}=0)}\left(g^{33}_{(\underline{q}=0)} + g^{3i}_{(\underline{q}=0)} T^{ij} g^{j3}_{(\underline{q}=0)}\right)\epsilon^{-1}_{(\underline{q}=0)}$$

where the last relation comes from another form of the Dyson equation, (4), and

$$T = \frac{C}{1-gC} .$$

From the relation (I.11) we have, for a homopolar crystal (Z = 0)

$$\epsilon^{-1} g^{33} = \gamma g^{22} \gamma \epsilon - 1$$

$$\epsilon^{-1} g^{32} = \gamma g^{22}$$

which apply in q-space as well as in real space. At $q = 0$ g^{31} vanishes when summed over the sublattices. Thus

$$\chi \propto Y g^{22} Y + \left[1 - Y g^{22} Y e\right]^2_{(q=0)} T^{33}$$

$$+ \left[Y g^{22}_{(q=0)}\right]^2 T^{22} - 2\left[1 - Y g^{22} Y e\right]_{(q=0)} T^{23} Y g^{22}_{(q=0)}. \quad (7)$$

In the absorption, the first term, which is summed over both sublattices, makes no contribution.

We consider (7) in a few simple cases. The most natural is that in which the defect mass and charge are changed, but not the polarizability, $\Delta Y = \Delta T = 0$ in (I.10). Then

$$C = \begin{pmatrix} -\omega^2 \Delta M & 0 & \Delta Z \\ 0 & 0 & 0 \\ \Delta Z & 0 & 0 \end{pmatrix}$$

and

$$T = \frac{1}{D} \begin{pmatrix} -\omega^2 \Delta M + \Delta Z g^{33} \Delta Z & 0 & \Delta Z (1 - g^{13} \Delta Z) \\ 0 & 0 & 0 \\ \Delta Z (1 - g^{13} \Delta Z) & 0 & \Delta Z g^{11} \Delta Z \end{pmatrix}$$

where $D = \omega^2 \Delta M g^{11} + (1 - \Delta Z g^{13})^2 - g^{11} g^{33} \Delta Z^2$ is the determinant of $1 - gC$, and the Green's functions are at the origin of real space. In this case only one term remains in (7)

$$\chi \propto \left[1 - Y g^{22} Y e\right]^2_{(q=0)} T^{33}$$

$$g_m \chi \propto \left[1 - Y g^{22} Y e\right]^2_{(q=0)} g_m T^{33} \quad (8)$$

In the case of $\Delta Z = 0$ in D, T^{33} simply gives the usual absorption by a charged defect in a lattice of neutral atoms

$$g_m T^{33} = g_m \Delta Z G'' \Delta Z = g_m \frac{\Delta Z g'' \Delta Z}{1 - \omega^2 \Delta M g''}$$

as in Dawber & Elliott (1963a). Of course, (8) is not the simple result of Dawber & Elliott because our model allows the change in the defect charge to appear in the denominator, D, and thus to affect the position of the localized mode or resonance. A second consequence of the ΔZ dependence of the denominator is a modification of the simple ΔZ^2 form of the (integrated) intensity.

From (2) and (3) we see that $Y g^{22}_{(q=0)} Y$ is the susceptibility due to electronic (shell) motion, which the cores are too massive to follow and for which $u = 0$ in (I.2). At $q = 0$ for a transverse vibration,

$$\epsilon = -\frac{4\pi}{3}$$

and so the factor in (8) is $\left(1 + \frac{4\pi}{3}\chi\right)^2 = \Lambda$, the Lorentz correction.

As a second simple case of (7), we consider a changed polarizability but $\Delta M = \Delta Z = 0$. (We consider $\Delta M = 0$ for ease of solving the example, the point of which is to show that the correction factor is altered when $\Delta Y \neq 0$.) The T-matrix which results from (I.10) is

$$\frac{1}{D}\begin{pmatrix} 0 & 0 & 0 \\ 0 & \Delta T + \Delta Y g^{33} \Delta Y & \Delta Y - \Delta Y g^{23} \Delta Y \\ 0 & \Delta Y - \Delta Y g^{23} \Delta Y & \Delta Y g^{22} \Delta Y \end{pmatrix}$$

where $D = -\Delta K g^{22} + (1-\Delta Y g^{23})^2 - g^{22} g^{23} \Delta Y^2$. (Again, the Green's functions in T are those at the origin of real space, where the defect is located. If we write in (7)

$$g^{22} = \sum_{\underline{q}} g^{22}(\underline{q})$$

$$g^{23} = Y \sum_{\underline{q}} \epsilon(\underline{q}) g^{22}(\underline{q})$$

$$g^{33} = Y^2 \sum_{\underline{q}} \epsilon(\underline{q}) g^{22}(\underline{q}) \epsilon(\underline{q}) - \sum_{\underline{q}} \epsilon(\underline{q})$$

we obtain

$$\chi \propto \frac{1}{D} \left\{ \Delta Y^2 \sum_{\underline{q}} \left[1 - Y^2 g^{22}_{(\underline{q}=0)} \left(\epsilon_{(\underline{q}=0)} - \epsilon_{(\underline{q})} \right) \right]^2 g^{22}_{(\underline{q})} \right.$$

$$\left. -2 \left(\sqrt{\Lambda}\, \Delta Y \right) g^{22}_{(\underline{q}=0)} + \left[Y g^{22}_{(\underline{q}=0)} \right]^2 \Delta T \right\} \qquad (9)$$

where Λ is the Lorentz factor of (8), and the factor in square brackets in the coefficient of ΔY^2 is seen to be related to Λ . This result corresponds with (49) in Hartmann & Elliott (1967) apart from the factors mentioned, which are introduced by our model. (Our special case, $\Delta M = 0$, corresponds to their $C^{11} = 0$). Again, even apart from the correction factors, our result is not exactly that of Hartmann & Elliott, because our model allows a ΔY dependence of the denominator, giving a change in the position of the localized mode or resonance due to changes in the charge-dependent forces coupling the defect with the rest of the lattice.

The result of combining the two special cases we have discussed can be thought of as leading to a ΔY -dependent modification of the Lorentz factor. This full case will be discussed in the next chapter, in application to silicon. The appearance of the Lorentz factor in (8) and, in modified form, in (9) and in the general case reduces the importance of the mechanism suggested by Leigh & Szigeti, which was mentioned in Section II.1. This will also be discussed in the next chapter, in application to silicon.

II.4.1. The Absorption Mechanism of Leigh & Szigeti

Leigh & Szigeti (1967a) consider the "apparent charge", η_n induced on the nth atom of the host lattice by the electric field, $\underline{E}$, of a charged defect

$$\eta^{\alpha}_{\alpha n} = \frac{\partial M_\alpha}{\partial u_{n\alpha}} = \frac{\partial}{\partial u_{n\alpha}} \int P_\alpha \, dv$$

where $\underline{M}$ is the total dipole moment of the crystal, $\underline{u}_n$ the displacement of the nth atom and the polarization, $\underline{P}$, at a particular point, is

$$4\pi \underline{P} = (\epsilon - 1) \cdot \underline{E}$$

Far from the defect, where the dielectric constant, ϵ , has the value for the perfect crystal, $\epsilon = \epsilon_0 + \epsilon_1$ and $\underline{E} = \underline{E}_0 + \underline{E}_1$, where ϵ_0 , $\underline{E}_0$ are the values at zero displacement, and ϵ_1 , $\underline{E}_1$ are due to atomic displacement. Of these terms, there will be a contribution to η only from ϵ_1 , $\underline{E}_1$, and Leigh & Szigeti select only one term:

$$\eta^{x}_{\alpha n} = \frac{1}{4\pi} \frac{\partial}{\partial u_{n\alpha}} \int (\epsilon_1 \cdot \underline{E}_0)_x \, dv \qquad (10)$$

The two ways in which the dielectric constant can depend on the motion of the lattice, in first order, are as a linear function of the strains (a coupling with the acoustical modes, the source of Brillouin scattering), and as a linear function of the relative displacements of the sublattices (a coupling with the optical modes). Leigh & Szigeti find that in silicon the former produces a much smaller effect than the latter, and we consider it no further. For long-wavelength optical modes in a lattice having diamond structure, they define a "Raman constant", β , in terms of the relative displacement $\underline{q} = \underline{u}_{(A)} - \underline{u}_{(B)}$ of the two sublattices A, B:

$$\epsilon_0^2 \beta = \frac{\partial \epsilon_{xy}}{\partial q_z} = \frac{\partial \epsilon_{yz}}{\partial q_x} = \frac{\partial \epsilon_{zx}}{\partial q_y}$$

Then (10) becomes, far from the impurity,

$$\eta^{x}_{\alpha n} = \pm \frac{\epsilon_0^2 V_{at} \beta}{2\pi} \sum_{\gamma} E_\gamma \epsilon_{x\alpha\gamma} \qquad (11)$$

where V_{at} is the volume per atom, $\epsilon_{x\alpha\gamma}$ is 0 if any of its subscripts are the same and 1 otherwise (see e.g. Smith, 1948), and the sign in front depends on which sublattice n is on. The field is just the Coulomb field, depending on the distance, $\underline{r}_n$, of the site n from the impurity charge, $e\Delta Z$

$$\underline{E} = e\Delta Z \frac{\underline{r}_n}{\epsilon_0 r_n^3} \, . \qquad (12)$$

II.4.2. Application to the Linear Chain

In their paper, Leigh & Szigeti go on to work out the total apparent charge induced in the crystal by their effect, and use this to estimate the absorption caused throughout the crystal by the presence of a charge. They consider their treatment to be valid for apparent charges a reasonable distance away from the defect; calculations for regions closer to the defect being disturbed by possible spreading of the defect charge, short-range polarization forces, and the change in the dielectric constant at the defect. The latter two are taken explicitly into account by the microscopical Shell model. Since, according to (3), the absorption is proportional to $\sum_{ij} Z_i g_{ij} Z_j$ where Z_i can be shell, ionic or apparent charges, it is important to consider cross-terms between these different types of charge as well as the squared terms. The linear diatomic chain gives some insight into this and into the frequency dependence of the sums involving Leigh & Szigeti's apparent charges.

We consider a perfect diatomic linear chain, with masses m, M and force-constant matrix A, and on one of the sites we shall place a charge, $e\Delta Z$. This problem can be solved exactly for a simple Shell model, but since the dynamics are given by the perfect lattice Green's function and hence the terms in the shell charge vanish when summed over the perfect lattice, we consider directly the Born model to which the Shell model reduces. A block-diagonalizes to A_θ , giving the

secular equation

$$\begin{vmatrix} \frac{2}{m} - \frac{\omega^2}{\gamma} & -\frac{2}{\sqrt{mM}}\cos\theta \\ -\frac{2}{\sqrt{mM}}\cos\theta & \frac{2}{M} - \frac{\omega^2}{\gamma} \end{vmatrix} = 0 \qquad -\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2}$$

from which

$$\frac{\omega^2}{\gamma} = \left(\frac{1}{m} + \frac{1}{M}\right) \pm \sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4\sin^2\theta}{mM}} \quad ,$$

where γ is the force constant.

If we write $M = m/\rho^2$, $0 < \rho^2 < 1$, and consider the frequencies at $\theta = 0$, $\theta = \frac{\pi}{2}$, we can define

$$\omega_0^2 = 0 \qquad (\theta = 0, \text{ acoustic})$$
$$\omega_1^2 = \frac{2\gamma}{m}\rho^2 \quad (\theta = \frac{\pi}{2}, \text{ acoustic})$$
$$\omega_2^2 = \frac{2\gamma}{m} \qquad (\theta = \frac{\pi}{2}, \text{ optic})$$
$$\omega_3^2 = \frac{2\gamma}{m}(1+\rho^2) \quad (\theta = 0, \text{ optic})$$

Then

$$\theta = \sin^{-1}\sqrt{\frac{\omega^2(\omega_3^2 - \omega^2)}{\omega_1^2\,\omega_2^2}}$$

and

$$\frac{dq}{d\omega^2} = \frac{1}{2r_0} \sqrt{\frac{\omega_3^2 - 2\omega^2}{\omega^2(\omega_1^2 - \omega^2)(\omega_2^2 - \omega^2)(\omega_3^2 - \omega^2)}} \qquad (13)$$

where $\theta = qr_0$ and r_0 is the distance between neighbours. The

eigenvectors, $(x_\pm , y_\pm)$ for optical (+) and acoustical (-) modes are, if $\omega^2 = \omega_-^2 = \omega_3^2 - \omega_+^2$,

$$x_- = y_+ = \sqrt{\frac{\omega_1^2 - \omega^2}{\omega_3^2 - 2\omega^2}}$$

$$y_- = x_+ = \sqrt{\frac{\omega_2^2 - \omega^2}{\omega_3^2 - 2\omega^2}}$$

which satisfy the orthonomality relations

$$(x_i \; y_i)\begin{pmatrix} x_j \\ y_j \end{pmatrix} = \delta_{ij}$$

and closure

$$x_-^2 + x_+^2 = y_-^2 + y_+^2 = 1$$

$$x_- y_- + x_+ y_+ = 0$$

The singularity at $\omega^2 = \omega_3^2/2$ occurs in the middle of the gap, and does not arise physically.

Using these results, we can obtain the imaginary part of the diatomic linear chain Green's function.

$$\mathrm{Im}\, g(\omega^2; \ell\ell') = \mathrm{Im} \frac{1}{N} \sum_{|q|} \begin{pmatrix} x_- & x_+ \\ y_- & y_+ \end{pmatrix} \frac{1}{\omega_{q\mp}^2 - \omega^2 + i\epsilon} \begin{pmatrix} x_- & y_- \\ x_+ & y_+ \end{pmatrix} \cos q(r_\ell - r_{\ell'})$$

where ϵ is a small imaginary part which enables us to replace the denominator by delta-functions, using

$$\lim_{\epsilon \to 0} \frac{1}{x + i\epsilon} = P\left(\frac{1}{x}\right) - i\pi\delta(x)$$

where P denotes principle part. After replacing the summation over the wave-vector $|q|$ by an integration over frequency, which is

possible in this case since $\omega^2(q)$ is a one-to-one function,

$$\frac{1}{N}\sum_{|q|} \rightarrow \frac{r_0}{\pi}\int_0^{q_m} dq \rightarrow \frac{r_0}{\pi}\int_0^{\omega_m^2} \frac{dq}{d\upsilon^2}\, d\upsilon^2 ,$$

we have

$$\begin{aligned} g_m g(\omega^2; \ell\ell') = & -r_0\int_0^{\omega_1^2} d\upsilon^2 \frac{dq}{d\upsilon^2}\begin{pmatrix} x_- \\ y_- \end{pmatrix}\delta(\upsilon^2-\omega^2)(x-y_-)\cos q(\upsilon^2)(r_\ell - r_{\ell'}) \\ & -r_0\int_{\omega_3^2}^{\omega_2^2} d\upsilon^2 \frac{dq}{d\upsilon^2}\begin{pmatrix} x_+ \\ y_+ \end{pmatrix}\delta(\upsilon^2-\omega^2)(x_+ y_+)\cos q(\upsilon^2)(r_\ell - r_{\ell'}) \\ = & -r_0\frac{dq}{d\omega^2}\left\{\begin{pmatrix} x_-^2 & x_-y_- \\ y_-x_- & y_-^2 \end{pmatrix}+\begin{pmatrix} x_+^2 & x_+y_+ \\ y_+x_+ & y_+^2 \end{pmatrix}\right\}\cos q(\omega^2)(r_\ell - r_{\ell'}) \\ = & -r_0\frac{dq}{d\omega^2}\cos q(\omega^2)(r_\ell - r_{\ell'})\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \end{aligned}$$

(14)

where the integration from 0 to ω_3^2 is broken up by using the antisymmetry of $dq/d\omega^2$ under $\omega_-^2 \rightarrow \omega_+^2$, and the last identity uses the closure relations for the eigenvectors. In more complicated cases, where moving from one phonon branch to another does not cause so simple a transformation of $dq/d\omega^2$, there is a frequency dependence in the matrix part of (14), which will be important in the frequency dependence of Leigh & Szigeti's absorption.

We now consider this absorption, supposing the Raman constant in (11), β, to be a number with sign differing on the two sublattices, $\beta = \beta(1,-1)$. The squared term is (κ,κ' refer to the sublattices)

$$\sum_{\substack{\ell\kappa \\ \ell'\kappa'}}{}' \eta\begin{pmatrix}\ell \\ \kappa\end{pmatrix} g_m g(\omega^2; \begin{matrix}\ell\ell' \\ \kappa\kappa'\end{matrix}) \eta\begin{pmatrix}\ell' \\ \kappa'\end{pmatrix} \propto \sum_{\ell\ell'}{}' \frac{\cos 2\theta(\omega^2)(\ell-\ell')}{\ell^2 \ell'^2}$$

where the prime means that the defect site is excluded, and the form of $\mathcal{Im}\, g$ enables us to separate the sums over the two sublattices. We can evaluate the sum by breaking it into

$$\left[\sum_{\ell}{}' \frac{\cos 2\theta(\omega^2)\,\ell}{\ell^2}\right]^2$$

where ℓ is integer or half-integer according to whether or not we are concerned with the sublattice containing the defect. Using the result

$$\sum_{-\infty}^{\infty} f(n) = -\{\text{sum of residues of } \pi\cot\pi z f(z) \text{ at the poles of } f(z)\},$$

we have for these respective sublattices

$$S_1 \equiv 2\Theta^2(\omega^2) + \frac{\pi^2}{3}$$

and

$$S_2 \equiv 2\Theta^2(\omega^2) + \frac{13\pi^2}{12} \tag{15}$$

as the value of $\sum_{\ell}{}' \cos 2\theta(\omega^2)\,\ell/\ell^2$.

We can now write the absorption

$$\mathcal{A}(\omega) \propto \omega\left\{\sum_{\substack{\ell K\\ \ell' K'}}{}' \eta\begin{pmatrix}\ell\\K\end{pmatrix}\mathcal{Im}\, g(\omega^2;\begin{smallmatrix}\ell\ell'\\KK'\end{smallmatrix})\eta\begin{pmatrix}\ell'\\K'\end{pmatrix} + 2\sum_{\ell K}{}' \eta\begin{pmatrix}\ell\\K\end{pmatrix}\mathcal{Im}\, g(\omega^2;\begin{smallmatrix}\ell 0\\K 0\end{smallmatrix})\, e\Delta z + (e\Delta z)^2\,\mathcal{Im}\, g(\omega^2;\begin{smallmatrix}00\\00\end{smallmatrix})\right\}$$

$$= -\frac{1}{2}\frac{e^2\Delta z^2(\omega_3^2-2\omega^2)}{\sqrt{(\omega_1^2-\omega^2)(\omega_2^2-\omega^2)(\omega_3^2-\omega^2)}}\left\{(1\ 0)\begin{pmatrix}1\\0\end{pmatrix} + 2\left(\frac{V_{at}\epsilon_0\beta}{2\pi r_0^2}\right)(S_1-S_2)\begin{pmatrix}1\\0\end{pmatrix} + \left(\frac{V_{at}\epsilon_0\beta}{2\pi r_0^2}\right)^2 (S_1-S_2)\begin{pmatrix}S_1\\-S_2\end{pmatrix}\right\}$$

from (11), (12), (13), (14) and (15), where the sign of β is undetermined (experimental measurements have found only its magnitude in silicon and

germanium). Since this leaves the sign of the middle term undetermined we do not know whether the Leigh & Szigeti mechanism will increase or reduce the absorption in this system. However, where the two sublattices are indistinguishable, as in the diamond structure, and there is equal chance of a defect appearing on either sublattice, the middle term has added to it another in which the vector describing the defect site is (0, 1), and that describing the apparent charge is $(S_2, -S_1)$. Thus the cross-terms vanish and the Leigh & Szigeti mechanism enhances the absorption. This argument generalizes by symmetry to real diatomic lattices, and it also applies to the cross-term with the shell charges when the Shell model is applied to an imperfect lattice.

We then have $K(\omega) \propto$

$$-e^2 \Delta z^2 r_0 \omega \frac{dq}{d\omega^2} \left\{ 1 + \left(\frac{V_{at} \epsilon_0 \beta}{2\pi r_0^2} \right)^2 \left[\left(2\Theta^2(\omega^2) + \frac{\pi^2}{3} \right)^2 + \left(2\Theta^2(\omega^2) + \frac{13\pi^2}{12} \right)^2 \right] \right\} \tag{16}$$

As ω^2 goes from 0 to ω_1^2 (or ω_3^2 to ω_2^2), 2Θ varies from 0 to π. If we insert values for silicon (see e.g. Leigh & Szigeti, 1967a) in the factor in front of the square brackets, it becomes $\sim .35$ and the Leigh & Szigeti mechanism contributes from ~ 40 to ~ 120 times as much as ordinary absorption. This is very large, and the reason is that we have assumed the Raman tensor to have diagonal components, while it has in fact only off-diagonal components. The coupling between mutally perpendicular vibrations is a second-order

effect in a linear chain in three dimensions with central forces, so it is reasonable to expect β to be effectively an order of magnitude smaller than we have used. This reduces the above numbers by two orders of magnitude, putting them in rough agreement with the results of Leigh & Szigeti. Finally, as we have seen in section II.3, the polarizability of the host atoms introduces the Lorentz factor in the usual absorption mechanism in an imperfect lattice. Thus for (16) to apply to a realistic model, in which a change in charge on one site leads to changed mass and force constants, the shell charges, Y , would augment the first term in the curly brackets by the Lorentz factor, which is 21 in silicon. Thus the Leigh & Szigeti absorption varies, depending on the frequency, from 2% to 6% of the usual absorption, described by Dawber & Elliott (1963a).

CHAPTER III

ABSORPTION BY SILICON WITH LIGHT AND HEAVY DEFECTS

III.1. The infrared absorption by defects in silicon were studied theoretically by Dawber & Elliott (1963b) as an application of their earlier paper (1963a) discussing the general theory of defects vibrating in crystals and especially the vibrational amplitudes. The theory allows a change of mass at the defect site, but neglects changes in the force constants. They considered charged defects of groups III and V, both lighter and heavier than the silicon atoms, and showed that the absorption intensity produced by the vibrating charge is proportional to the density of states of the perturbed lattice. This they were able to calculate from a perfect lattice density of states, using a Green's function method of the sort described in the previous chapter. They suggested an experiment to check the theory in which equal amounts of a group III and a group V impurity were dissolved in silicon, providing electrical compensation to eliminate free carrier absorption. This experiment was carried out by Angress, Goodwin & Smith (1965), who used B^- and P^+ impurities, achieving final exact electrical compensation by fast electron bombardment, introducing a controllable number of trapping centres. They found close agreement with the theory for the boron localized mode frequencies, assuming a 10% force constant change, and for the localized mode intensity, assuming unit charge on the boron and no local field correction. Phosphorus, however, produces a resonance which

is displaced from the frequency indicated by the theory, and the intensity of the absorption by the band modes is about 2.5 times larger than that predicted for isolated impurities carrying a unit charge. The theoretical error in frequency cannot be explained by a force constant change of the same order as that involved in boron, and Angress et al. suggest aggregation of impurities and spreading of the defect charge as possible explanations. A distributed charge could also account for the discrepancy in intensity, although they suggest that a local field correction could apply in this case.

Experimental work on the localized mode produced by carbon in silicon is reported by Newman & Willis (1965), who compare the intensity of this absorption with Dawber & Elliott's theory and with the preliminary results of Smith & Angress (1963) for boron. They find this intensity to be five times that of boron.

Leigh & Szigeti (1967a) suggest the mechanism of defect-induced "apparent charges", described in the previous chapter, to account for the unexpected largeness of the band mode integrated intensity observed by Angress et al. By estimating the resulting charge at the defect, on the nearest neighbours, and throughout the rest of the lattice, they arrive at an overall effect in boron and phosphorus doped silicon which is 2.4 times that due to the impurities alone. Following the experimental result on boron localized modes, they assume that there is no local field correction to the effect due to the impurities alone.

In the present chapter we obtain results for Leigh & Szigeti's effect based on a microscopical calculation, and show this contribution for a small region of the band. We consider the absorption in this region due to charged phosphorus, antimony and thallium defects. A consideration of the localized modes due to boron and carbon defects show that we are able to fit the experimental results in both these cases, although the meaning of the parameters used is not yet clear.

III.2. Silicon, Structure and Force Constants

Silicon occurs having the diamond structure, which consists of a face-centred cubic lattice with two identical atoms per unit cell, each with a tetrahedral environment. These may be considered to be located at (0, 0, 0) and at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ a in the unit cell. For silicon, a = 2.35 Å.

Since we shall be interested only in changes occurring at the defect site itself, we need not consider the symmetry properties of its neighbours. We do, however, need the symmetry operations of the perfect lattice to establish the force constants and to calculate the Green's functions. These are contained in the translation group of the f. c. c. lattice, together with the tetrahedral point group, T_d, and inversion coupled with a nonprimitive translation, which exchanges the two sub-lattices. The latter two, however, can be combined into an effective point group, O_h, when we perform symmetry operations on the dynamical matrix, provided that we use q-values in the interior and not on the boundary of the Brillouin zone (Lax, 1960: Ch. 19H.). Using this,

we can calculate the Green's function, as described in section I.3.

The short-range force constants used, taken out to second neighbours, have the same form for core-core, core-shell, and shell-shell coupling, typically:

Nearest neighbours

$$\Phi\begin{pmatrix}0 & 0\\ 1 & 2\end{pmatrix} = \begin{pmatrix}a & b & b\\ b & a & b\\ b & b & a\end{pmatrix}$$

Second neighbours

$$\Phi\begin{pmatrix}0 & 110\\ 1 & 1\end{pmatrix} = \begin{pmatrix}c & e & -y\\ e & c & -y\\ y & y & d\end{pmatrix}$$

$$\Phi\begin{pmatrix}0 & 110\\ 2 & 2\end{pmatrix} = \begin{pmatrix}f & h & -x\\ h & f & -x\\ x & x & g\end{pmatrix}$$

These lead to typical terms in the dynamical matrix of section I.2.

$$D^{11}_{xx} = k + 4c\cos q_x[\cos q_y + \cos q_z] + 4d\cos q_y \cos q_z$$

$$D^{11}_{xy} = -4e\sin q_x \sin q_y + 4iy\sin q_z[\cos q_x - \cos q_y]$$

$$D^{12}_{xx} = 4a\left[\cos\tfrac{q_x}{2}\cos\tfrac{q_y}{2}\cos\tfrac{q_z}{2} + i\sin\tfrac{q_x}{2}\sin\tfrac{q_y}{2}\sin\tfrac{q_z}{2}\right]$$

$$D^{12}_{xy} = -4b\left[\sin\tfrac{q_x}{2}\sin\tfrac{q_y}{2}\cos\tfrac{q_z}{2} - i\cos\tfrac{q_x}{2}\cos\tfrac{q_y}{2}\sin\tfrac{q_z}{2}\right]$$

with D^{22} the same as D^{11} if $k \to l, c \to f, d \to g, e \to h, y \to z$. The conditions (I.1) require that for core-core and core-shell (in centre-of-mass coordinates)

$$k = -4a - 8c - 4d$$

$$l = -4a - 8f - 4g$$

In the shell-shell case, an extra term arises from the isotropic force, K , connecting each shell to its own core, and

$$k = -4a - 8c - 4d + K$$

$$l = -4a - 8f - 4g + K$$

The values used for these parameters are taken from Dolling & Cowley (1966) who fitted the model to neutron scattering data. They give in units of 10^4 dyne/cm :

$$a_R = a_S = -12.338$$

$$a_T = 1.364\ a_R$$

$$b_R = 0.214\ a_R$$

$$b_S = -.009\ a_S$$

$$b_T = -.328\ a_T$$

$$\mu = 0.4176$$

$$\gamma = 1.2666$$

$$\nu = -.4711$$

$$\delta = -.9792$$

where $c_R = f_R = c_S = f_S = \mu$, $c_T = f_T = 1.364\mu$, $e_R = h_R = e_S = h_S = \nu$, $d_R = g_R = d_S = g_S = \gamma$, $d_T = g_T = 1.364\gamma$, $x_T = y_T = 1.364\delta$, $e_T = f_T = 1.364\nu$, $x_R = y_R = x_S = y_S = \delta$. These identifications have been made without physical justification in order to reduce the number of parameters.

The values for the core-shell force constant

$$K = 68.58\ 10^4 \text{ dyne/cm}$$

and for the shell charge

$$Y = -2.865 \text{ proton charges}$$

are from Dolling & Cowley's determination of Π, d in the relations

$$\Pi = \frac{\gamma^2}{K+4a_T} \qquad d = \frac{-\gamma \cdot 4a_T}{K+4a_T}$$

The long-range Coulomb forces of section I.2 have been prepared by C.T. Sennett, and are incorporated into the calculations after the manner of Page & Strauch (1968). (See (I.11)).

The resulting Green's functions are tabulated in the Appendix for those frequency values for which they have been calculated.

III.3. Band Modes and the Leigh & Szigeti Terms

To get some idea of the size and frequency dependence of the Leigh & Szigeti absorption, we calculate the sums

$$\sum_{\ell K \alpha} \eta_\alpha^\kappa \begin{pmatrix} \ell \\ K \end{pmatrix} g_{\alpha\beta}^{ij} \begin{pmatrix} \ell & 0 \\ K & 0 \end{pmatrix} \tag{1}$$

and

$$g_m \sum_{\substack{\ell K \alpha \\ \ell' K' \beta}} \eta_\alpha^\kappa \begin{pmatrix} \ell \\ K \end{pmatrix} g_{\alpha\beta}^{11} \begin{pmatrix} \ell & \ell' \\ K & K' \end{pmatrix} \eta_\beta^\kappa \begin{pmatrix} \ell' \\ K' \end{pmatrix}$$

which recur in the expression for the absorption in section II.3,

$$\chi = \frac{e^2}{V} \sum_{\substack{\ell K \alpha i \\ \ell' K' \beta j}} Z_\alpha^i \begin{pmatrix} \ell \\ K \end{pmatrix} G_{\alpha\beta}^{ij} \begin{pmatrix} \ell & \ell' \\ K & K' \end{pmatrix} Z_\beta^j \begin{pmatrix} \ell' \\ K' \end{pmatrix} \tag{2}$$

where G is related to g by the Dyson equation, (II.4). This we do, in

the computer program used for evaluating g, by changing the sum over real space to one over q-space, and adding it up over the sample of q-values that are used in finding g. Since $\eta^{\kappa}_{\alpha n}$ has a Coulomb dependence on the site $n=(\ell,\kappa)$, given by (II.10), we have

$$\eta^{\kappa}_{\alpha}\left(\frac{q}{\kappa}\right) = \frac{1}{4}(-)^{\kappa} e^{-i\underline{q}\cdot\underline{r}_{\kappa}} \frac{iq_{\gamma}}{q^2} \epsilon_{\kappa\alpha\gamma}\, \epsilon_{0\beta\gamma}\, \Delta z\, e \qquad (3)$$

where the phase factor comes from Fourier transforming and the other terms are defined in (II.11) and (II.12).

The summands in (1) diverge at the origin of q-space as $1/q$ and $1/q^2$, but the sums themselves do not diverge, and in the first case the contribution from the origin vanishes. We rely on the close distribution of q-points (see Appendix) to give us reasonably accurate values. This procedure breaks down at $\omega = 0$, where we have to cope in addition with the divergence of the Green's functions. However, we know the absorption to be proportional to ω (see (II.1)), and so it is not necessary to perform the calculation at $\omega = 0$.

The sums become

$$\sum_{q\kappa\alpha} \eta^{\kappa}_{\alpha}\left(\frac{q}{\kappa}\right) P^{-1\,ij}_{\alpha\beta}\left(\frac{q}{\kappa\, 0}\right)$$

$$= iC \sum_{|q|} \frac{1}{q^2} \sum_{\kappa} (-)^{\kappa} \sum_{s} \sum_{\alpha\gamma} \left\{ e^{-iS\underline{q}\cdot\underline{r}_{\kappa}} \Delta^{-1\,ij}_{s\alpha s\beta}\left(\frac{q}{\kappa 0}\right) - e^{iS\underline{q}\cdot\underline{r}_{\kappa}} \Delta^{-1\,ji}_{s\beta s\alpha}\left(\frac{q}{0\kappa}\right) \right\} \epsilon_{\kappa s\alpha} s_{\gamma}$$

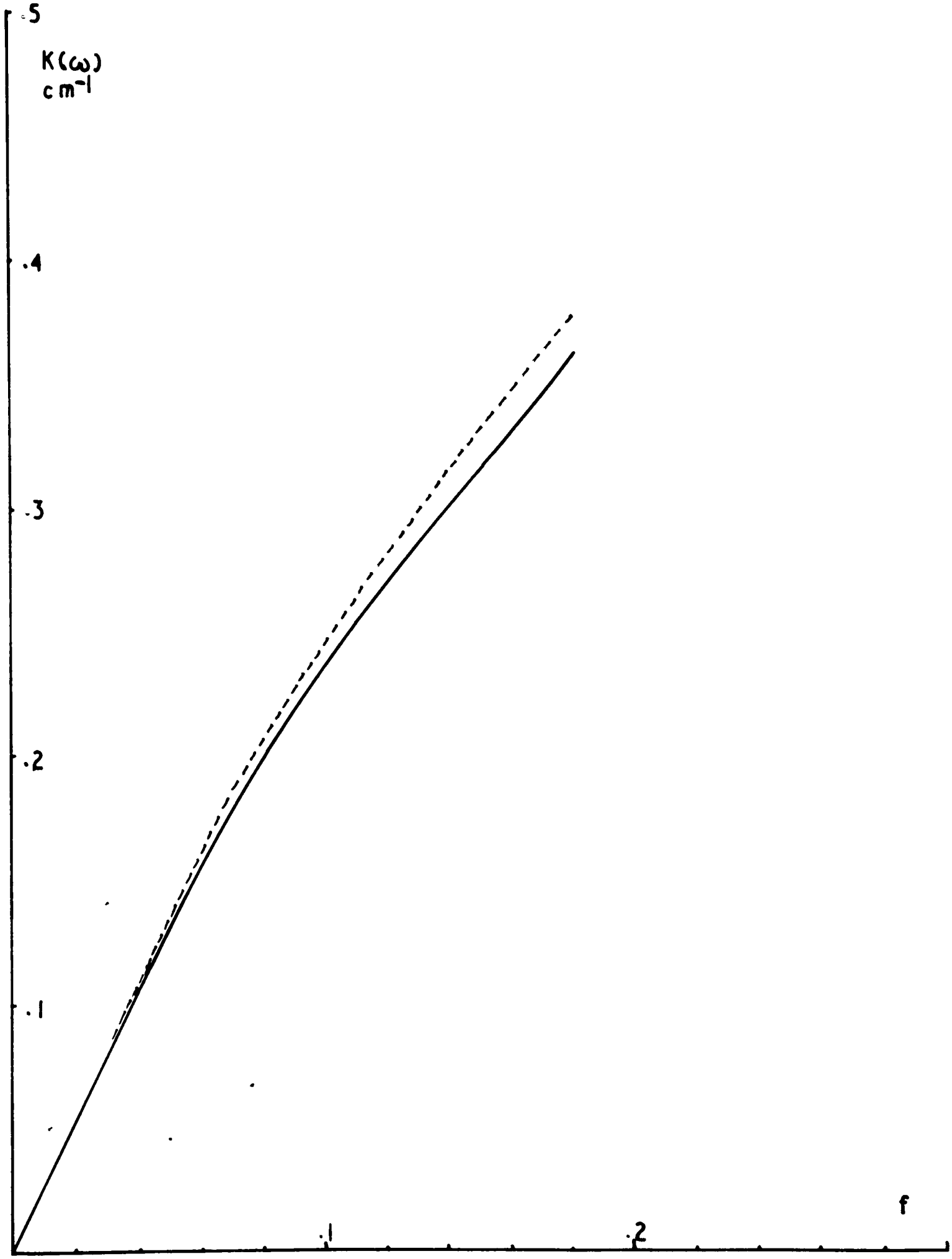


Fig. III.1. Si:P⁺. Concentration = .1% Dashed line shows absorption including Leigh & Szigeti effect.

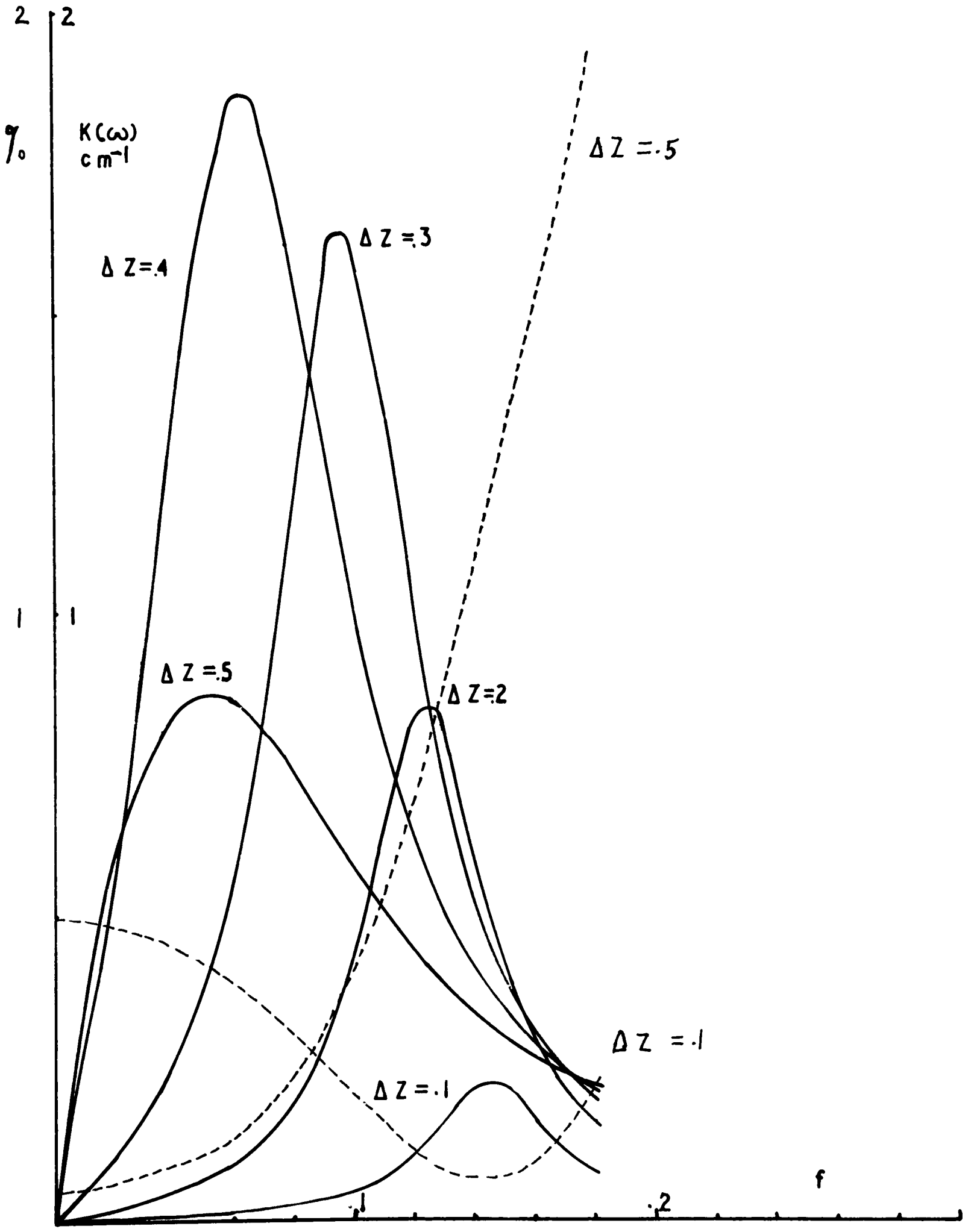


Fig. III.2. Si:Sb resonant modes for various ΔZ. Concentration = .1% Dashed curves give Leigh & Szigeti effect as a percentage of the remaining absorption (solid curves), to be added to the solid curves.

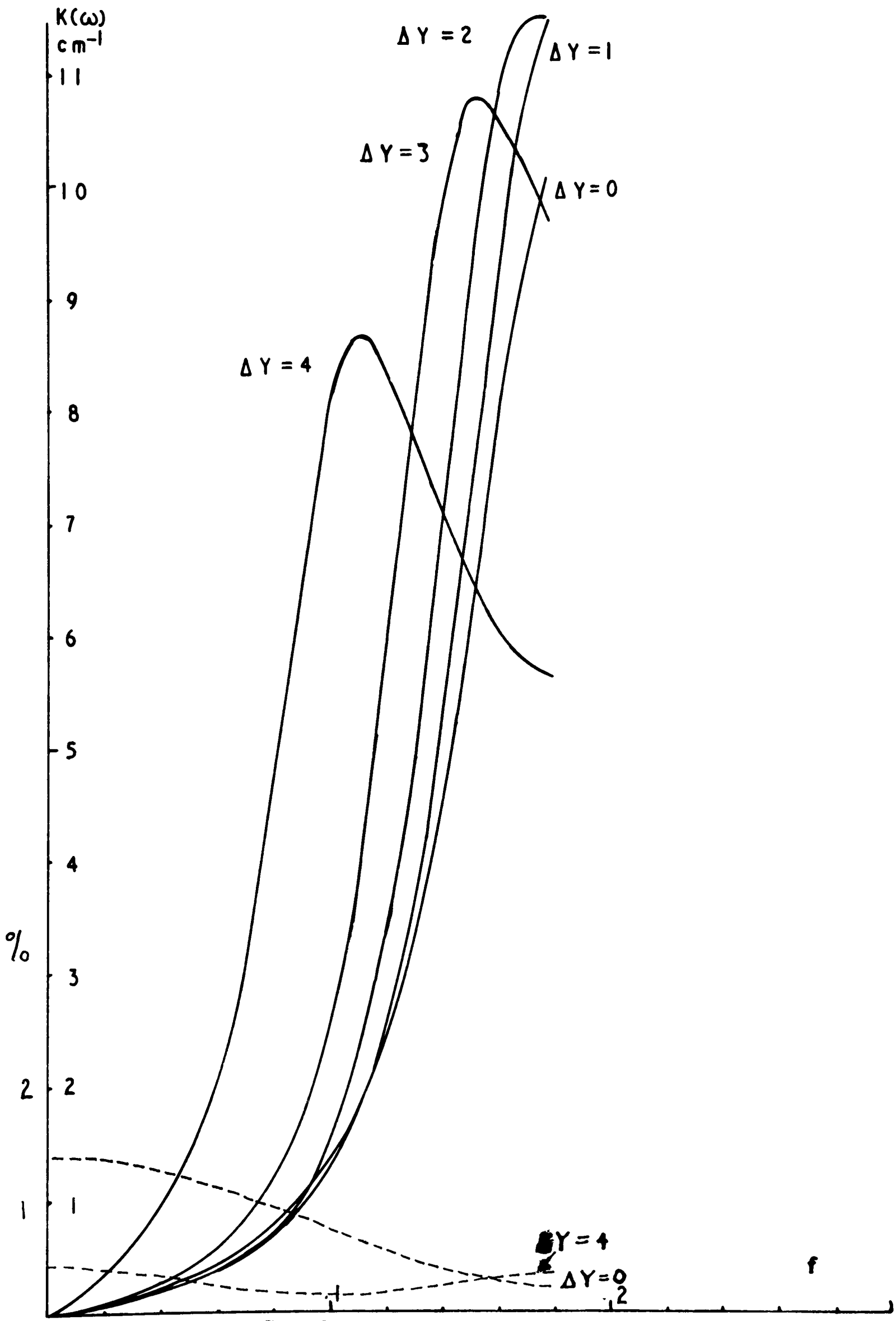


Fig. III.3. Si:Tl⁻ resonant modes for various ΔY. Concentration = .1% Dashed curves give Leigh & Szigeti effect as a percentage, as in Fig. III.2.

and $$\sum_{qKK'\alpha\beta} \eta^{\chi}_{\alpha}\left(\frac{q}{K}\right) P''_{\alpha\beta}\left(\frac{q}{K K'}\right) \eta^{*\chi}_{\beta}\left(\frac{q}{K'}\right)$$

$$= C^2 \sum_{|q|} \frac{1}{q^4} \sum_{KK'} (-)^{K+K'} \sum_{S} \sum_{\alpha\beta\gamma\delta} \left\{ e^{-iS\underline{q}\cdot\underline{r}_{KK'}} \Delta^{-1\,\prime\prime}_{S\alpha S\beta}\left(\frac{q}{KK'}\right) + e^{iS\underline{q}\cdot\underline{r}_{KK'}} \Delta^{-1\,\prime\prime}_{S\beta S\alpha}\left(\frac{q}{K'K}\right) \right\}$$

$$\times \epsilon_{\chi S\alpha S\gamma} \epsilon_{\chi S\beta S\delta} q_{S\gamma} q_{S\delta}$$

where $C = \frac{1}{4} \epsilon_0 \beta r_0 \Delta Z e$ and the complex conjugation on η refers only to the phase factor. The other symbols are used in (3) or in (I.8) and (I.9). These are the expressions that are calculated by the computer program.

In Figures 1, 2, 3 we plot the absorption due to P^+, Sb^+, and Tl^- in the bottom fifth of the band, showing the Leigh & Szigeti contribution. The points between those tabulated in the Appendix were obtained by a quadratic interpolation on the perfect lattice Green's function and on the Leigh & Szigeti terms. The original values of the Green's functions and the interpolated values were then used to obtain the absorption, using the results of section II.2.

In Fig. 2, showing the results for antimony, (group V, mass 122) we see the effect of changing the defect charge on the resonance. As $\Delta Z \to 0$, the position of the resonance approaches that predicated by Dawber & Elliott (1963b). As ΔZ becomes larger, the resonant frequency decreases until the vanishing of the absorption at $\omega = 0$ begins to dominate the ΔZ^2 variation of the intensity. In Fig. 3,

we fix the charge of the thallium defect (group III, mass 204) and show the dependence of the resonance on ΔY.

To our knowledge, there is no experimental work on these defects in silicon. The particular region of the band was chosen because it is likely to be the smoothest and most free from absorption peaks due to the perfect lattice. We did not investigate the rest of the band because of the large amount of computer time required to calculate our special Green's functions, and because of the uncertainty of the significance of the parameters ΔT and ΔY (see next section), the understanding of which will require, we feel, more experimental work on localized modes.

III.4. Localized Modes

We now apply our theory to the experiental results for carbon and boron defects in silicon. First we examine in more detail the effects of varying the parameters ΔZ, ΔY, ΔT of section II.3. This examination depends on the results of computer experiments, and so the discussion that follows is but a rough justification of these results.

The frequency of the localized mode depends on the zeros of the determinant of $1-gC$ in (II.5). From (I.8), $g^{ij} = g^{ji}$.

$$0=|1-gC| = \begin{vmatrix} 1-g^{11}A - g^{13}\Delta Z & -g^{12}\Delta K - g^{13}\Delta Y & -g^{11}\Delta Z - g^{12}\Delta Y \\ -g^{12}A - g^{23}\Delta Z & 1-g^{22}\Delta K - g^{23}\Delta Y & -g^{12}\Delta Z - g^{22}\Delta Y \\ -g^{13}A - g^{33}\Delta Z & -g^{13}\Delta K - g^{33}\Delta Y & 1-g^{13}\Delta Z - g^{23}\Delta Y \end{vmatrix} \quad (4)$$

where the notation is that of (I.11) except $A = -\Delta M \omega^2$, and the second equality follows using (I.10) in the definition of C in section I.3 with $\Delta R = \Delta S = 0$, $\Delta T = \Delta K$. This determinant contains a constant term, and terms in ΔK , ΔY , ΔY^2 , ΔZ, $\Delta Y \Delta Z$, ΔZ^2, $\Delta Y^2 \Delta Z$, $\Delta Y \Delta Z^2$ $\Delta K \Delta Y$, $\Delta K \Delta Y \Delta Z$, Λ of which the last four cancel out in the expansion. We now consider an approximate analytical form for g^{ij} in the region above the band.

From (I.11), we see that the real parts of g^{11}, g^{12} and g^{13} have the form

$$\sum \frac{a_i}{\omega^2 - b_i} \simeq \frac{\sum a_i + \cdots}{\omega^2 - \sum b_i + \cdots} = \frac{a}{\omega^2 - b}$$

where the ~~last~~ first follows if ω^2 is larger than all the b_i . This is the case if we are in the region well above the band. Similarly, g^{22}, g^{23}, g^{33} are of the form

$$\sum a_i \frac{\omega^2 - c_i}{\omega^2 - b_i} \simeq a \frac{\omega^2 - c}{\omega^2 - b}$$

The imaginary parts, of course, vanish, according to section II.2. These forms enable us to interpolate between the computed values of g^{ij} above the band listed in the appendix. We have

$$g^{11} = \frac{2.017 \times 10^{-6}}{f^2 - .587} \quad \text{cm/dyne}$$

$$g^{12} = -\frac{7.89 \times 10^{7}}{f^2 - .592} \quad \text{cm/dyne}$$

$$g^{13} = \frac{5.55 \times 10^{-2}}{f^2 + 1.026}$$

$$g^{22} = -1.395 \times 10^{-6} \; \frac{f^2 - .937}{f^2 - .693} \quad \text{cm/dyne} \qquad (5)$$

$$g^{23} = -1.053 \times 10^{-1} \; \frac{f^2 - .646}{f^2 - .399}$$

$$g^{33} = -3.96 \times 10^{4} \; \frac{f^2 - .728}{f^2 - .537} \quad \text{dyne/cm}$$

where $f = \omega/\omega_{MAX}$ and we have arbitrarily taken $\omega_{MAX} = 2\pi \times 16.0 \times 10^{12}$ rad./sec. (The experimental value for silicon is 0.0644 ev. or 15.57×10^{12} c.p.s. (Angress et al, 1965).) The forms (5) are used in all computations of the localized modes.

Expanding the determinant (4) shows that the coefficients of all the terms containing ΔZ go to zero at large f, using (5). For a small range of f, these terms can be said to vary as 1/ (f + constant). the coefficients of the other terms go as $\sim$ constant + 1/(f + constant). Then we can write for (4)

$$0 = \{\text{const.}, \Delta K, \Delta Y, \Delta Y^2, \Delta Z, \Delta Y \Delta Z, \Delta Z^2, \Delta K \Delta Z^2\}$$

$$\simeq (\text{const.}, \Delta K, \Delta Y, \Delta Y^2)$$

$$+ [\text{const.}, \Delta K, \Delta Y, \Delta Y^2, \Delta Z, \Delta Y \Delta Z, \Delta Z^2, \Delta K \Delta Z^2] \; \frac{1}{f_L + \text{const.}}$$

where the brackets indicate linear combinations of their contents. Thus

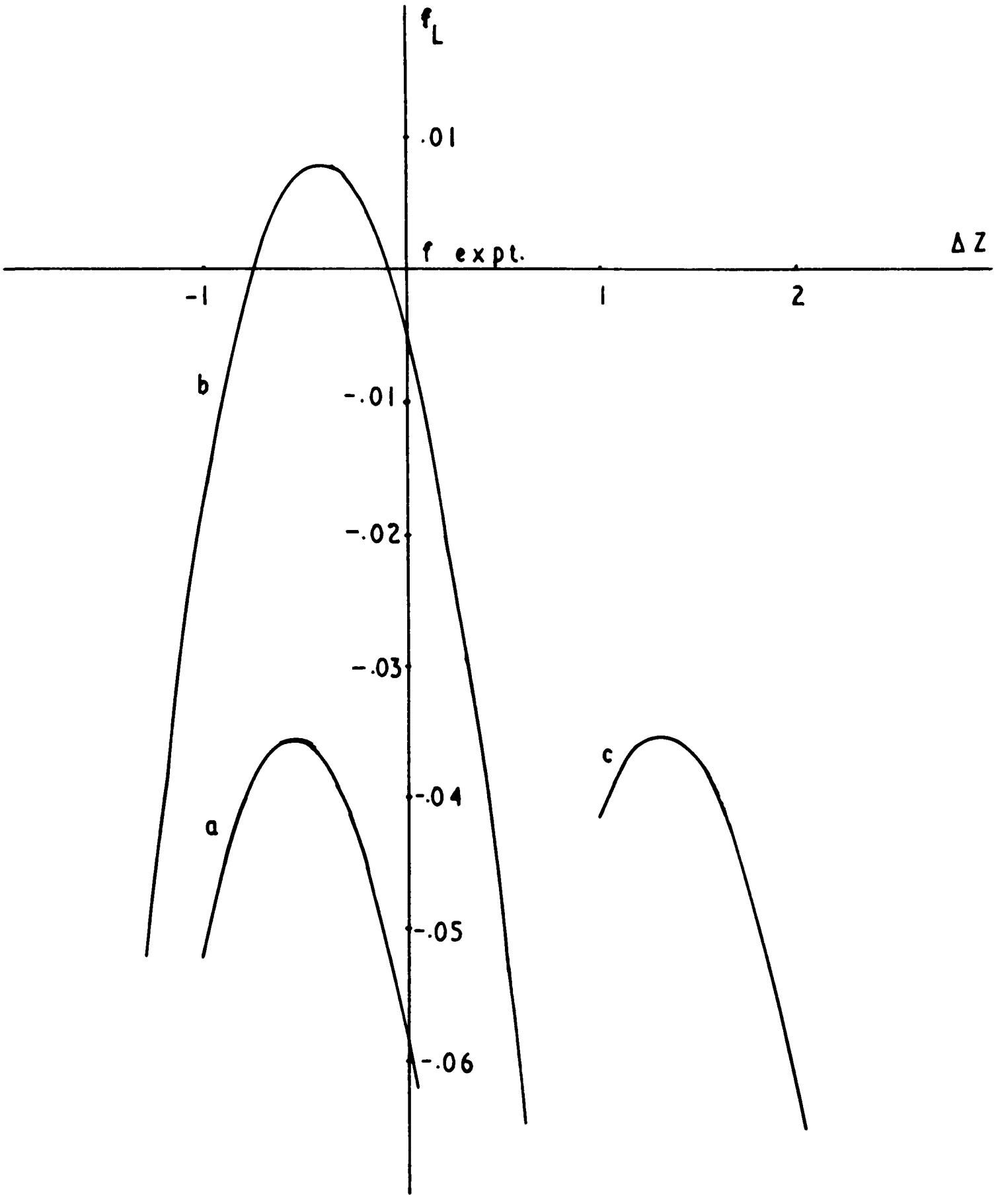


Fig. III.4. Localized mode frequency, Si: ^{10}B, vs. ΔZ.
a) $\Delta Y=0$, $\Delta K=-2x10^5$. b) $\Delta Y=0$, $\Delta K=-1x10^5$. c) $\Delta Y=4$, $\Delta K=-2x10^5$

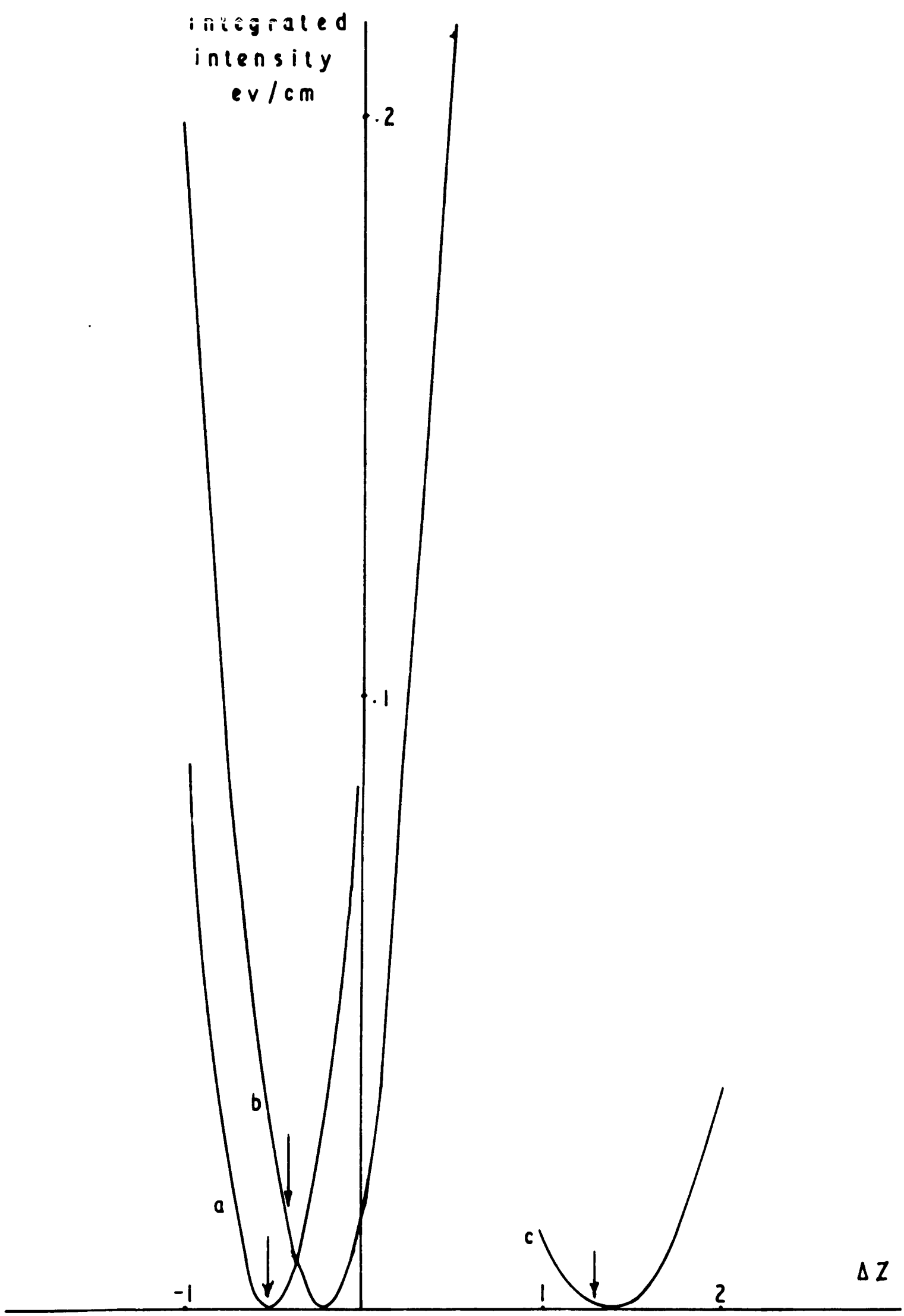


Fig. . . ntegrated intensity vs ΔZ for Si:$^{10}B^{-}$.
a) Δ =0, Δ -1x1 . b) Δ , Δ -1x1 . c) Δ , Δ -2x1 .
Concentration - .1347. Apex position shown for parabolas of Fig. III.4.

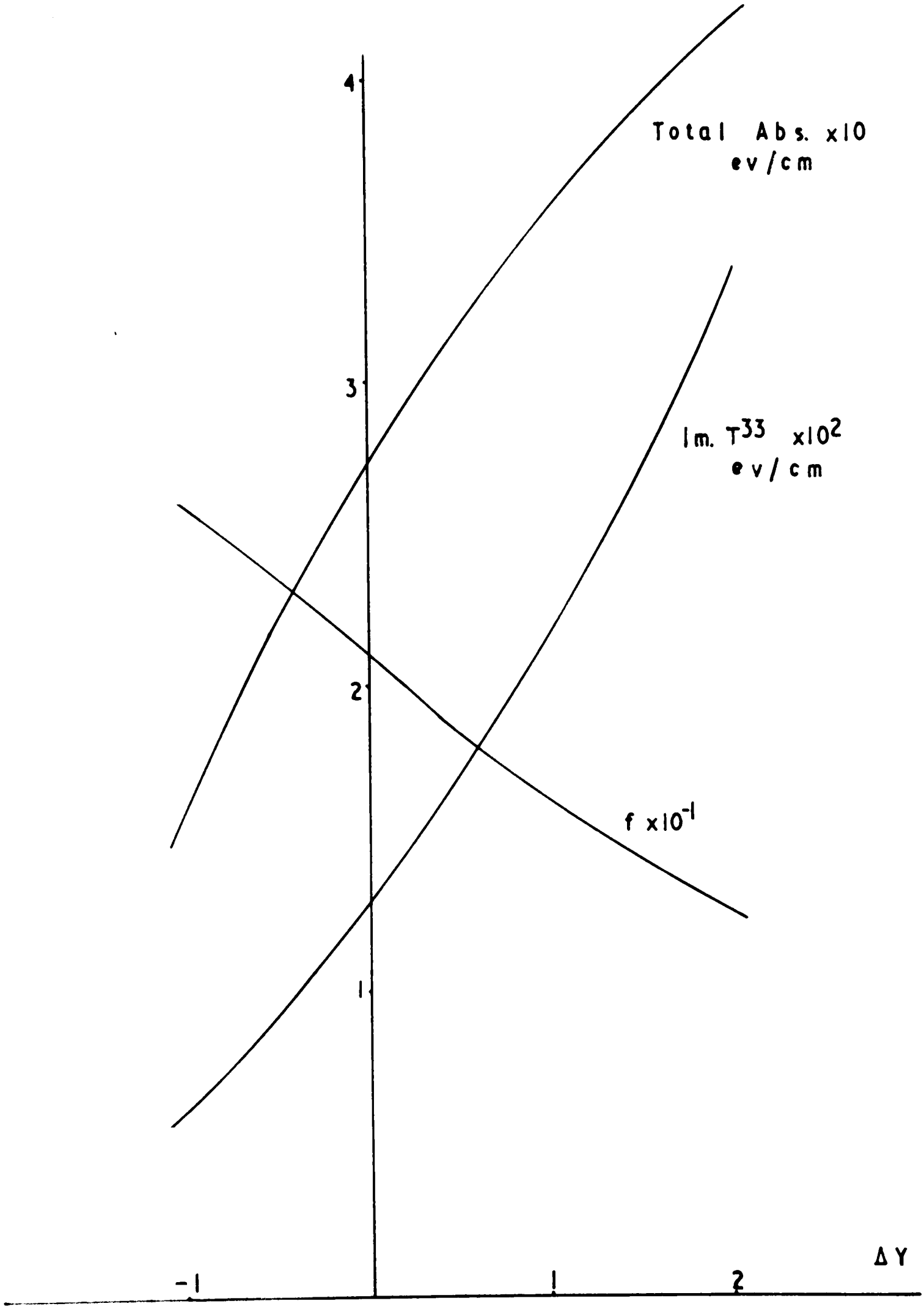


Fig. III.6. Integrated intensity. Si: $^{11}B^-$ with $\Delta Z=-1$, $\Delta K=0$, concentration= .0184%. Plotting Im T^{33}, f, fxIm T^{33} as functions of Y. NB. $f(\Delta Y=o) = \Lambda$.

if we further suppose the coefficients of $\Delta K, \Delta Y, \Delta Y^2, \Delta K \Delta Z^2$ to be small,

$$f_L + const \simeq -\frac{1}{(const)} [const, \Delta K, \Delta Y, \Delta Y^2, \Delta Z, \Delta Y \Delta Z, \Delta Z^2]$$

This particular form gives a parabolic dependence of f_L on ΔZ such that if ΔK is changed the parabola shifts linearly up and down along the f-axis, and if ΔY is changed it shifts from side to side along the ΔZ -axis. This behaviour is shown (see Fig. 4) by the computed parameter-dependence of the localized mode frequency.

Fig. 5 shows the expected quadratic dependence of the integrated intensity on ΔZ for the same three sets of values $(\Delta Y, \Delta K)$.

The modification of the Lorentz factor due to ΔY, discussed in section II.3, is shown in Fig. 6. The integrated intensity resulting from $g_m T^{33}$ must be multiplied by a factor f to obtain the observed integrated intensity. When $\Delta Y = 0$, $f = \Lambda$, the Lorentz factor of (II.8).

We may compare the results for boron and carbon with earlier theories and with experiment. The table shows the localized mode frequencies predicted by various theories for the two isotopes of boron when $\Delta Z = 0$ (present notation). Angress et al. used the theory of Dawber & Elliott, but with a recalculated density of states. The numbers given for the frequencies are to be multiplied by 16.0×10^{12} ra./sec.

	Dawber & Elliott	Angress et al.	Present work
^{11}B	1.24	1.190	1.190
^{10}B	1.29	1.236	1.241

All these values are somewhat higher than the experimental results, and it is natural to use our theory to change the defect charge to $\Delta Z = -1$. We have

	Present work	Experiment
^{11}B	1.162	1.162
^{10}B	1.214	1.207

The integrated intensity may be calculated for the ligher isotope at natural abundance in a boron content of 5×10^{19} cm^{-3}, using (II.1), (II.3), (II.6) applied to the first special case of section II.3.

$$\int d\omega\, K(\omega) = \pi \omega_M \frac{4\pi e^2 N \Lambda}{\eta c V} \frac{f_L a(f_L)}{d'(f_L)} \times \text{concentration}$$

where η is the index of refraction, c the velocity of light N the number of particles, V the crystal volume, $f_L \times \omega_M = \omega_L$ the localized mode frequency, Λ the Lorentz correction factor, d' the frequency derivative of $|1 - gC|$ and $a = T^{33} = \Delta Z^2 g''$. This gives

f_L	1.29	1.236	1.207
$\int d\omega\, K(\omega)$	.329	.287	.266 ev/cm.

These numbers are all of the order of Λ times the experimental result of Angress et al., .016 ev/cm. This is an unfortunate result, for the agreement between theory and experiment for the localized mode frequency and for the intensity, without the Lorentz factor, makes it appear that this factor should not be used.

What we must do, however, is to change the parameters ΔY and ΔK the effect of which is shown in figs. 4 and 5. The results are

summarized in the table. We also see that the experimental results of Newman and Willis for carbon in silicon can be fitted.

	Experiment		Present Work		Values of Parameters		
	f_L	$\int K$	f_L	$\int K$	ΔZ	ΔY	ΔK
^{10}B	1.207	.016	1.207	.016	.01	0.0	8.8×10^{4}
					- 1.0	- 1.75	-1.12×10^{5}
^{12}C	1.137	.080	1.137	.084	0.0	1.94	0.0

It is apparent from figs. 4 and 5 that the above parameters are not the only values which will fit the experimental results. Since the values of Y and K in the Shell model do not coincide very well with their conceptual meanings, the meanings of ΔY and ΔK above are not at all clear. The present theory leaves too much freedom to its parameters to give unique fits to experiment. However, both ΔY and ΔK are needed: boron cannot be fitted with $\Delta K = 0$, nor carbon with $\Delta Y = 0$, if ΔZ is to remain within a reasonable range (i.e. $\Delta Z = 0$ for carbon, $-1 \leq \Delta Z \leq 0$ for boron).

With this uncertainty, there is not much point in attempting a lengthy investigation of the band modes and resonances in the absence of further experimental results on light defects belonging to different chemical periods, from which it may be possible to work out an interpretation for ΔY and ΔK. We leave as the main result of this work the point that the absorption intensity and the Lorentz correction factor depend strongly on the polarizability of the defect as well as on that of the host lattice, and that these can be calculated with the assumptions usually made in the Shell model.

CALCIUM FLUORIDE

IV.1. Introduction

The technique of applying uniaxial stress to crystals containing colour centres was suggested by Kaplyanskii at a conference on luminiscence held in Moscow in 1958. His problem was to get around the macroscopic averaging out of the anisotropy of the individual centres, and he was able to use energy shifts due to uniaxial stress to distinguish four types of dipole absorption (linearly polarized electric and magnetic, and circularly polarized electric and magnetic) by three types of centres in a cubic crystal (oriented along the fourfold, threefold and twofold axes). He later did a phenomenological calculation of the magnitudes of the shifts, neglecting, however, the possibility of splitting of lines from individual centres due to the lowered symmetry. This case was treated by Schawlow, Piksis and Sugano, and a good discussion of the method, as far as it will concern us, is given by Gebhardt and Maier (1965), who deal with F-centres in alkali halides.

In the present work, the splitting by uniaxial stress of the localized vibrational mode of hydrogen and deuterium ions in calcium fluoride is used to determine some of the anharmonic forces coupling the defect to the host lattice. To do this we must go beyond the phenomenological theory of Gebhardt and Maier (whose treatment of the

excited p-state of the F-centre can be used directly for the localized mode problem, since only symmetry considerations are involved) and ~~constant~~ consider a microscopical theory. This is more easily done in the case of vibrational localized modes than with electronic colour centres, where a detailed knowledge of the structure, levels and wavefunctions of the centre, of the interaction with the lattice, of the nature of the localized deformation, etc. is difficult to obtain.

The splitting of a localized mode due to external stress is caused by the anharmonic force constants, which produce new harmonic terms when the neighbours of the defect relax under the applied stress. The essence of a microscopical theory, discussed in Section V.3. is a treatment of this relaxation in an imperfect lattice. The problem of relaxation about a defect in an unstressed crystal, due to the size of the defect, has been tackled by Ludwig, who divides the crystal into two regions. One region is remote from the defect and is assumed to behave like a continuum (or, what is equivalent, like a Bravais lattice); and the other region is in the neighbourhood of the defect, about which no assumptions are made other than those used here. Our treatment compares the imperfect lattice with the perfect and we arrive at the result (V. 15) , which is quite general for any crystal behaving according to the harmonic model. This approach also enables us to discuss the elastic constants of an imperfect crystal. which we do in the last chapter.

The microscopical theory developed in the following chapter for stress effects on localized modes is based on general considerations, but worked out in the case of calcium fluoride, for which we have experimental measurements (Elliott et al, 1965). We devote the remainder of this chapter to a discussion of this system. Calcium fluoride occurs naturally as the common mineral, fluorite. The name comes from the term "fluores lapides" of Georgius Agricola, who derives it from the latin verb for "to flow" because the mineral melts easily, referring to its use as a flux to dissolve impurities in the smelting of metals. It is found in the form of cubes, and in various colours, which confused its early identification (in the course of their works on minerals, both Albertus Magnus and Theophrastus describe stones which probably included fluorite, but neither they nor Agricola really identified it as a separate mineral), and led finally to an interest in it for physics. For the term "fluorescence" was coined by Stokes in a footnote to the paper (Phil. Trans. 142. 463, (1852)) which finally suggested the ultraviolet cause of an effect that had been known since the seventeenth century, and had shortly before been observed in some detail in fluorite by Sir David Brewster. (On the chemical side, another name, fluorine, was derived from the mineral because Ampere, in 1810, comparing with hydrogen chloride the gas produced by a reaction of sulphuric acid and fluorite, guessed at the presence of a new element). Impurities in the form of rare-earth elements were suggested by

G. Urbain in 1909 as a main source of fluorescence in natural fluorite, and he succeeded in synthesizing fluorite with traces of rare earth to test his idea. The techniques of growing synthetic crystals of CaF_2, without which recent research on it would have been impossible, were not finally developed until the second World War, when a programme of obtaining synthetic fluorite for optical purposes was undertaken at M.I.T., notably by Donald Stockbarger. The present work derives from a programme to study colour centres in CaF_2 (Elliott et al, 1965; Bessent, Hayes & Hodby, 1965), and results from the fact that the localized mode lines of hydrogen and deuterium introduced into the crystal are very sharp. (It is interesting to note that the original stress experiments of Kaplyanskii were done on luminescent rare earth centres in CaF_2.)

IV.2. Calcium Fluoride, Structure and Symmetry

Calcium fluoride crystallizes into a face-centred cubic lattice containing one calcium ion and two fluorine ions per unit cell. Each calcium ion is surrounded by eight fluorine ions, forming a cube about it, while each fluorine ion is in the centre of a tetrahedron of four calcium ions. The unit cell is usually chosen to be a rhombohedron of volume $v = 2r_o^3$ with basis vectors

$$\underline{a}_1 = r_o\,(0\ 1\ 1)$$

$$\underline{a}_2 = r_o\,(1\ 0\ 1)$$

$$\underline{a}_3 = r_o\,(1\ 1\ 0)$$

and lattice constant

$$2r_o = 5.45\ \text{Å}$$

When U-centres are created in a CaF_2 crystal, H^- and D^- ions substitute for the ions at fluorine sites, as has been shown by Elliott et al (1965), who point out that the transition to the second harmonic observed in the localized mode is compatible with a tetrahedral environment for the defect but not with a cubical environment. Thus, in considering the symmetry properties of the defect and it neighbours, we use the tetrahedral group T_d.

In order to simplify the calculations which follow, we shall need the symmetrized coordinate of the first and second nearest neighbours of the defect. These are the basis functions of the irreducible representations of T_d which contribute, and so our first step is to find out which these representations are. The space we wish to construct from these representations is the space spanned by all the possible displacements of the defect and its neighbours from equilibrium. A basis for this space consists of each of the $3(n + 1)$ displacements in the x, y or z directions of the defect and n neighbours. The character of each group element operating in this basis is the trace of the matrix which describes how the basis is transformed, and from the set of characters thus obtained, we can decompose the space uniquely into the irreducible representations it contains.

Thus, for the defect alone, the space is three-dimensional, and the decomposition is obviously into one representation only, which is Γ_5 of T_d.

	D	Ca_0	Ca_1	Ca_2	Ca_3	F_1	F_2	F_3	F_1'	F_2'	F_3'
Γ_5	1										
	1										
	1										
Γ_1		1 1 1	-1 -1 1	1 -1 -1	-1 1 -1						
Γ_3		1 1 -2	-1 -1 -2	1 -1 2	-1 1 2						
		-1 1 0	1 -1 0	-1 -1 0	1 1 0						
Γ_4		1 -1 0	-1 1 0	-1 -1 0	1 1 0						
		-1 0 1	-1 0 -1	1 0 1	1 0 -1						
		0 1 -1	0 1 1	0 -1 1	0 -1 -1						
Γ_5		0 1 1	0 1 -1	0 -1 -1	0 -1 1						
		1 0 1	1 0 -1	-1 0 1	-1 0 -1						
		1 1 0	-1 -1 0	-1 1 0	1 -1 0						
Γ_5		1	1	1	1						
		1	1	1	1						
		1	1	1	1						
Γ_1						1	1	1	-1	-1	-1
Γ_3						-2	1	1	2	-1	-1
							-1	1		1	-1
Γ_4						-1	-1	1	1	1	-1
						1	1	-1	-1	-1	1
Γ_4						1	-1	1	1	-1	-1
						-1	1	-1	-1	1	1
Γ_5						1	-1	1	-1	1	-1
						-1	1	-1	1	-1	1
						1	-1	-1	1	1	-1
Γ_5						1	1	1	1	1	1
						1	1	1	1	1	1
						1	1	1	1	1	1
Γ_5						1	1	1	1	1	1
						1	1	1	1	1	1
						1	1	1	1	1	1

Table IV.1. S_i transformation matrix to symmetrized co-ordinates for defect D, nearest neighbours, Ca_i and second neighbours, F_i. (Not normalized). The labels refer to Figure 1.

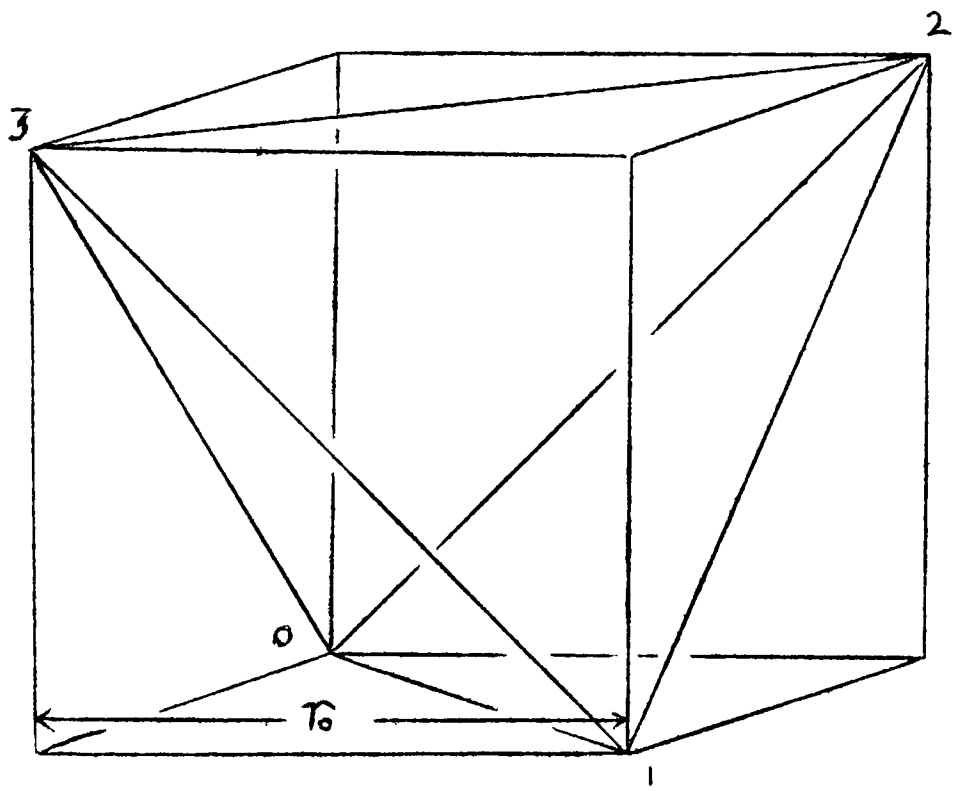


Figure IV. 1a. Ca nearest neighbours to U-centre.

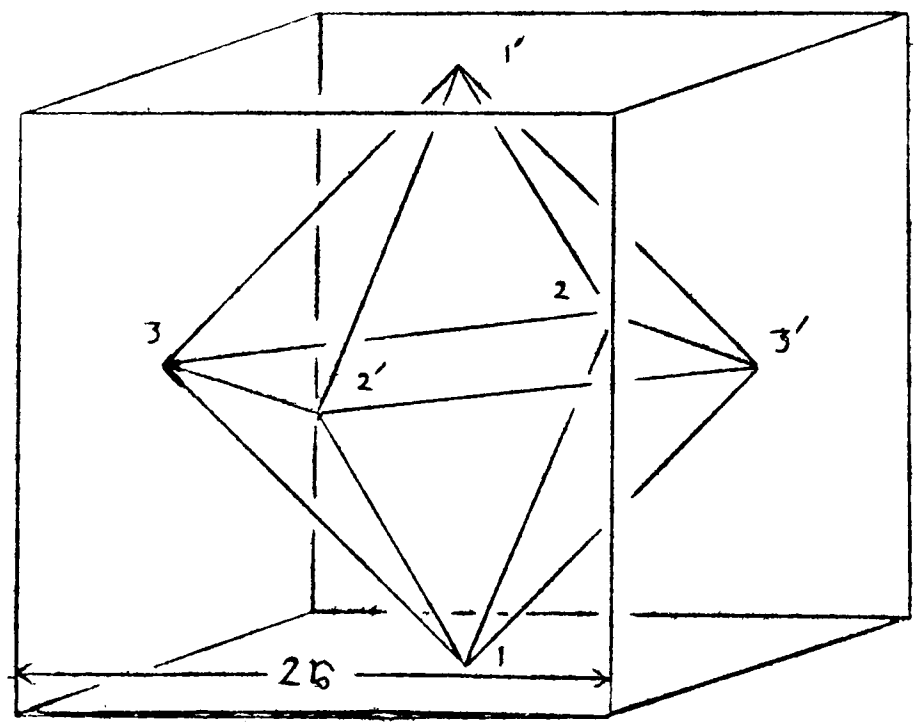


Figure IV. 1b. F second neighbours to U-centre.

For the shell of four nearest neighbours, the space has 12 dimensions, and

$$\Gamma_{n.n.} = \Gamma_1 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 .$$

For the shell of six next nearest neighbours, which form an octahedron about the defect, there are 18 dimensions, and

$$\Gamma_{2n.n.} = \Gamma_1 + \Gamma_3 + 2\Gamma_4 + 3\Gamma_5 .$$

We then have for the defect and its neighbours out to the second that the 33 x 33 matrix describing the force constants, or any other similar property (33 = 3 + 12 + 18) will decompose into:

one		2	x	2	matrix corresponding to the $2\Gamma_1$
two	identical	2	x	2	matrices $2\Gamma_3$
three	identical	3	x	3	matrices $3\Gamma_4$
three	identical	6	x	6	matrices $6\Gamma_5$

The transformation which effects this decomposition is the matrix, S, of basis functions (symmetrized coordinates), found by use of projection operators (see e.g. Tinkham, 1964) and guesswork, and given in Table 1.

It is also necessary to establish notation for the properties of the perfect lattice. We use the Born (rigid-ion) model and require the force constant matrix, $\Phi_{\alpha\beta}\binom{l\ l'}{\kappa\ \kappa'}$ (see e.g. Maradudin, Montroll & Weiss, 1963) coupling Cartesian component α of the displacement of the κ^{th} ion in the l^{th} unit cell with component β of the displacement

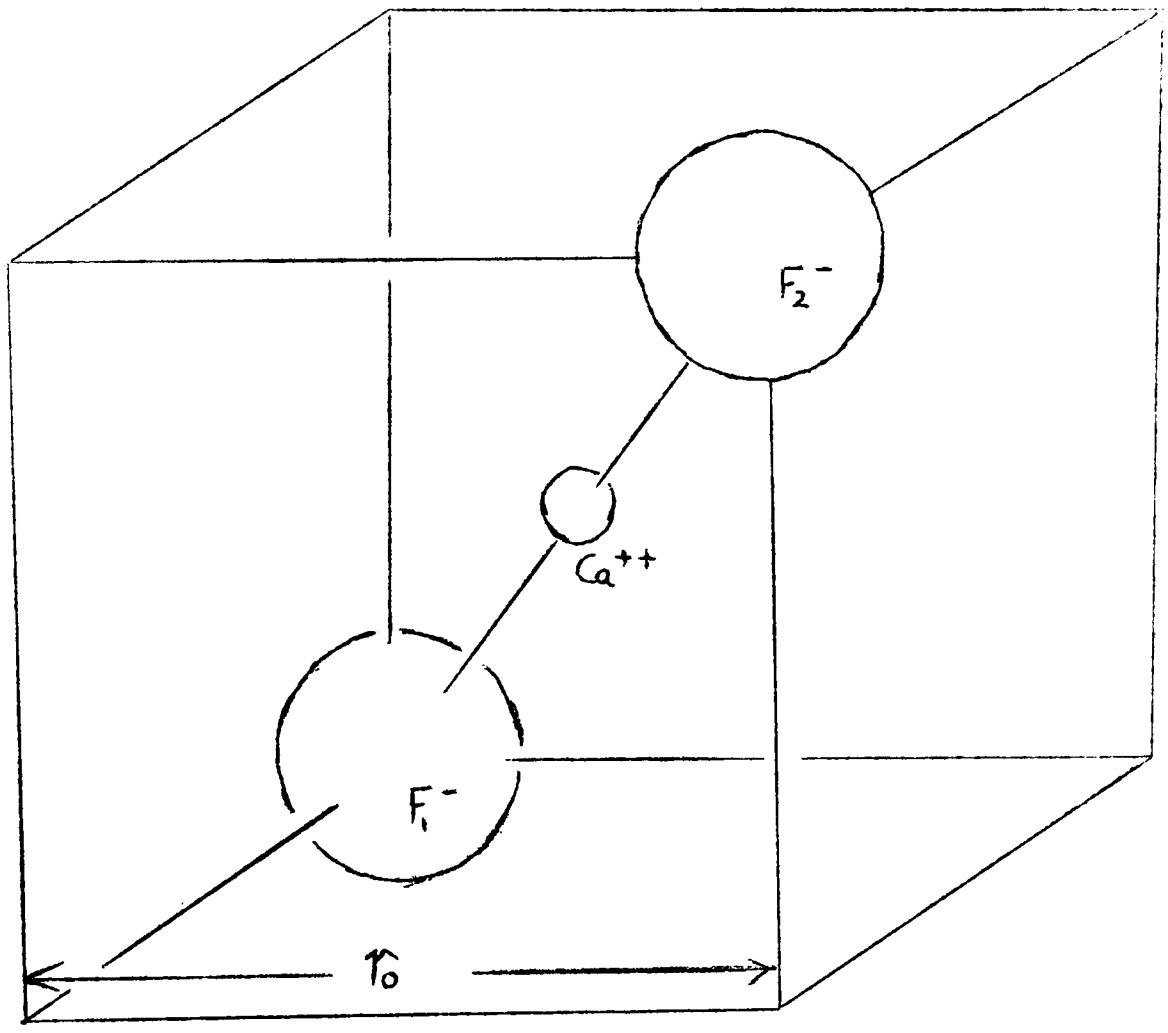


Figure IV. 2. Configuration of ions in the unit cell of CaF_2

of ion (ℓ',κ'). We shall also require the inverse of this, but since it refers to the same lattice, this has the same symmetry properties.

The force constant matrix, as pointed out in Chapter I, is composed of a short-range part, and a long-range Coulomb part. It is the former which appears explicitly most often in the calculations to follow, and so we now describe it in greater detail for CaF_2. We shall follow Sennett (1963) in considering the short-range part to extend only to third neighbours. The symmetry of the bonds limits the number of independent force constants, and we write the results below in their most general form,

Nearest neighbours. F_2 - Ca. Bond direction $(-1\,-1\,-1)\,\frac{r_0}{2}$.

$$\Phi\begin{pmatrix}0 & 0\\ F_2 & Ca\end{pmatrix} = \begin{pmatrix}a & b & b\\ b & a & b\\ b & b & a\end{pmatrix}.$$

Second neighbours. F_2 - F_1 . Bond direction $(-1\,0\,0)\,r_0$.

$$\Phi\begin{pmatrix}0 & 011\\ F_2 & F_1\end{pmatrix} = \begin{pmatrix}C & & \\ & A & B\\ & B & A\end{pmatrix}.$$

Third neighbours. Ca - Ca. Bond direction $(1\;1\;0)\,r_0$.

$$\Phi\begin{pmatrix}0 & 110\\ Ca & Ca\end{pmatrix} = \begin{pmatrix}c & e & \\ e & c & \\ & & d\end{pmatrix}.$$

Third neighbours. F - F. Bond direction $(1\;1\;0)\,r_0$.

$$\Phi\begin{pmatrix}0 & 110\\ F & F\end{pmatrix} = \begin{pmatrix}f & h & -x\\ h & f & -x\\ x & x & g\end{pmatrix}$$

The subscripts on the fluorine ions above are explained by Figure 2 .

Maradudin, Montroll & Weiss show that the condition of invariance of the force on each ion under translation gives

$$\sum_{l'K'} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ K & K' \end{pmatrix} = 0$$

and this gives us

$$\Phi\begin{pmatrix} 0 & 0 \\ Ca & Ca \end{pmatrix} = \begin{pmatrix} k & & \\ & k & \\ & & k \end{pmatrix}$$

where

$$k \equiv 8a + 8c + 4d$$

and

$$\Phi\begin{pmatrix} 0 & 0 \\ F & F \end{pmatrix} = \begin{pmatrix} l & & \\ & l & \\ & & l \end{pmatrix}$$

where

$$l \equiv 4a + 4A + 2C + 8f + 4g.$$

Sennett (1966) has evaluated these force constants by fitting the experiental elastic constants, the long-wave frequencies, and the dielectric constants at zero and infinite frequencies. He obtains, in units of 10^4 dyne/cm :

$$a = -1.684$$

$$b = -2.362$$

$$C = -1.644$$

$$A = 0.211$$

$$B = 0.0$$

$$c = e = f = h = 0.0467$$

$$d = g = x = 0.0$$

The identification of c, e, f, h, and the assigning of d, g, x to zero, are done before the fit is made, in order to reduce the number of parameters to be handled. A further parameter is the effective charge on the ions, which contributes to the observable quantities through the Coulomb interaction:

$$Z = 0.7789e$$

where Z is the charge on F^-, $-2Z$ on Ca^{++}.

In the matrix which represents the inverse of ϕ, the identifications made in the last paragraph do not hold, and while the independent constants up to third neighbours have the same symmetry as the force constants given above, non-zero constants also extend beyond third neighbours. The ones we shall need are, where $g \equiv \phi^{-1}$

$$g\begin{pmatrix} 0 & 002 \\ Ca & Ca \end{pmatrix} = \begin{pmatrix} \mu & & \\ & \mu & \\ & & \upsilon \end{pmatrix}$$

and

$$g\begin{pmatrix} 0 & 112 \\ F_i & Ca \end{pmatrix} = \begin{pmatrix} \alpha & \beta & \delta \\ \beta & \alpha & \delta \\ \epsilon & \epsilon & \gamma \end{pmatrix} .$$

We shall need to know g and φ, the change in ϕ due to a defect, in symmetrized form in the neighbourhood of the defect. φ has the same form as ϕ, considered, for our particular case, out to second neighbours. The symmetrized forms are obtained by constructing the

(33 x 33) matrices from the independent constants given above, and then transforming with S of Table 1 and its inverse. The results are:

$$\varphi_{\Gamma_1} = \begin{pmatrix} a+2b & & \\ & & c \end{pmatrix} \qquad g_{\Gamma_1} = \begin{pmatrix} z & y \\ y & z \end{pmatrix}$$

$$\varphi_{\Gamma_3} = \begin{pmatrix} a-b & & \\ & & c \end{pmatrix} \qquad g_{\Gamma_3} = \begin{pmatrix} u & v \\ v & s \end{pmatrix}$$

$$\varphi_{\Gamma_4} = \begin{pmatrix} a-b & & \\ & A & -B \\ & -B & A \end{pmatrix} \qquad g_{\Gamma_4} = \begin{pmatrix} r & q & p \\ q & n & \\ p & & j \end{pmatrix}$$

$$\varphi_{\Gamma_5} = \begin{pmatrix} -\ell & -\sqrt{8}b & -2a & 2B & -2A & -\sqrt{2}c \\ -\sqrt{8}b & a+b & \sqrt{2}b & & & \\ -2a & \sqrt{2}b & a & & & \\ 2B & & & A & -B & \\ -2A & & & -B & A & \\ -\sqrt{2}c & & & & & c \end{pmatrix}$$

$$g_{\Gamma_5} = \begin{pmatrix} \ell & \sqrt{8}b & 2a & -2B & 2A & \sqrt{2}c \\ & \omega & \sqrt{2}e & \psi & \chi & \varphi \\ & & \pi & \sigma & \xi & \kappa \\ & & & \rho & & \\ & & & & \Gamma & \sqrt{8}\epsilon \\ & & & & & \Delta \end{pmatrix} \quad \begin{matrix} + \text{transpose} \\ - \text{diagonal} \end{matrix} \qquad (1)$$

The new symbols which enter into the expressions for g are linear combinations of the independent constants above:

$z = k - 2c - 2e + d$ $\qquad w = l - 4h - \lambda$

$y = \sqrt{2}(a - 2b - \gamma - 2\delta)$

$u = k - 2c + d + e$ $\qquad s = l + 2h - \lambda$

$v = \sqrt{2}(a + b - \gamma + \delta)$

$r = k + e - d$ $\qquad n = l + 2h - \mu$

$q = \sqrt{2}(a + b + \epsilon - \alpha)$ $\qquad j = l - 2g + \mu$

$p = \sqrt{2}(\epsilon - \beta - 2b)$

$\omega = k - e - d$ $\qquad \rho = 2(l - 2h - \mu)$

$\psi = \sqrt{2}(\alpha + \epsilon + b - a)$ $\qquad \Gamma = l + 2g + \mu$

$\chi = \sqrt{2}(\beta + \epsilon)$ $\qquad \Delta = l + \lambda$

$\varphi = 2(\delta - \beta)$

$\pi = k + 2c + d$

$\sigma = 2(\beta - b)$

$\xi = 2(a + \alpha)$

$\varkappa = \sqrt{2}(a + \gamma)$

IV.3. U-Centres in Calcium Fluoride

As pointed out in the previous section, U-centres consist of H^- and D^- ions which in CaF_2 substitute for fluorine ions. The expressions for the force constants of CaF_2 have been derived, and hence for the change in force constants due to the defect, which have the same form. Such a change in force constants is necessary to fit the experimental value for the localized mode frequency: the assumption of a mass change alone leads to results which are 30% too high. We use

equation (4.14) of Elliott et al (1965) for the localized mode frequency.

$$\omega_L^2 = \frac{\Phi_{\alpha\alpha}\binom{0\ 0}{F_2\ F_1}\epsilon}{M_F(1-\epsilon)} + \sum_{\ell K\beta} \frac{\Phi_{\alpha\beta}\binom{0\ \ell}{F_2\ K}^2}{M_K\,\Phi_{\alpha\alpha}\binom{0\ 0}{F_2\ F_2}} \qquad (2)$$

where the notation for the force constants is that of the previous section, and $\epsilon = (M_F - M_{H(D)})/M_F$. In this case, Φ gives us the force constants in the imperfect lattice, including both short-range and Coulomb forces. The two experimental values for ω_L, one for H^- and one for D^-, allow us to fit two force-constant change parameters, which we take to be in the central nearest neighbour and central second neighbour forces. The difference between the two isotopic frequencies involves only the first term of (2), since the second term does not contain the defect mass. From this we have a relationship between $3a'$, the change in the n.n. central force constant, and C', the change in the 2 n.n. central force constant

$$2a' - C' \equiv K = 1.59 \times 10^4 \text{ dyne/cm}$$

This leaves one parameter, for which (2), a quadratic equation, can be solved. However, to obtain real solutions, it turns out to be necessary to change the charge on the defect, so that the change in the charge, $\zeta = (Z - Z')/Z$, lies in the range

$$-.56 \leq \zeta \leq -.26$$

This change alters the Coulomb part of Φ , and so the change in the force constants cannot be found until we know the effective charge at the defect site. This will be determined later, along with the anharmonic forces at the defect, by finding a best fit to experiental parameters. It must be pointed out here, however, that since it is only possible in practice to take a few terms in the sum of (2), and since the Coulomb force is long-range, inaccuracies arise in this part of the problem unless precautions are taken. The Page-Strauch formalism of the first part of this thesis cannot be used, for reasons discussed in Chapter I, since CaF_2 is an ionic crystal. It turns out, however, that we have sufficient information to determine the anharmonic forces with the present method.

EFFECTS OF EXTERNAL FIELDS ON LOCALIZED MODES

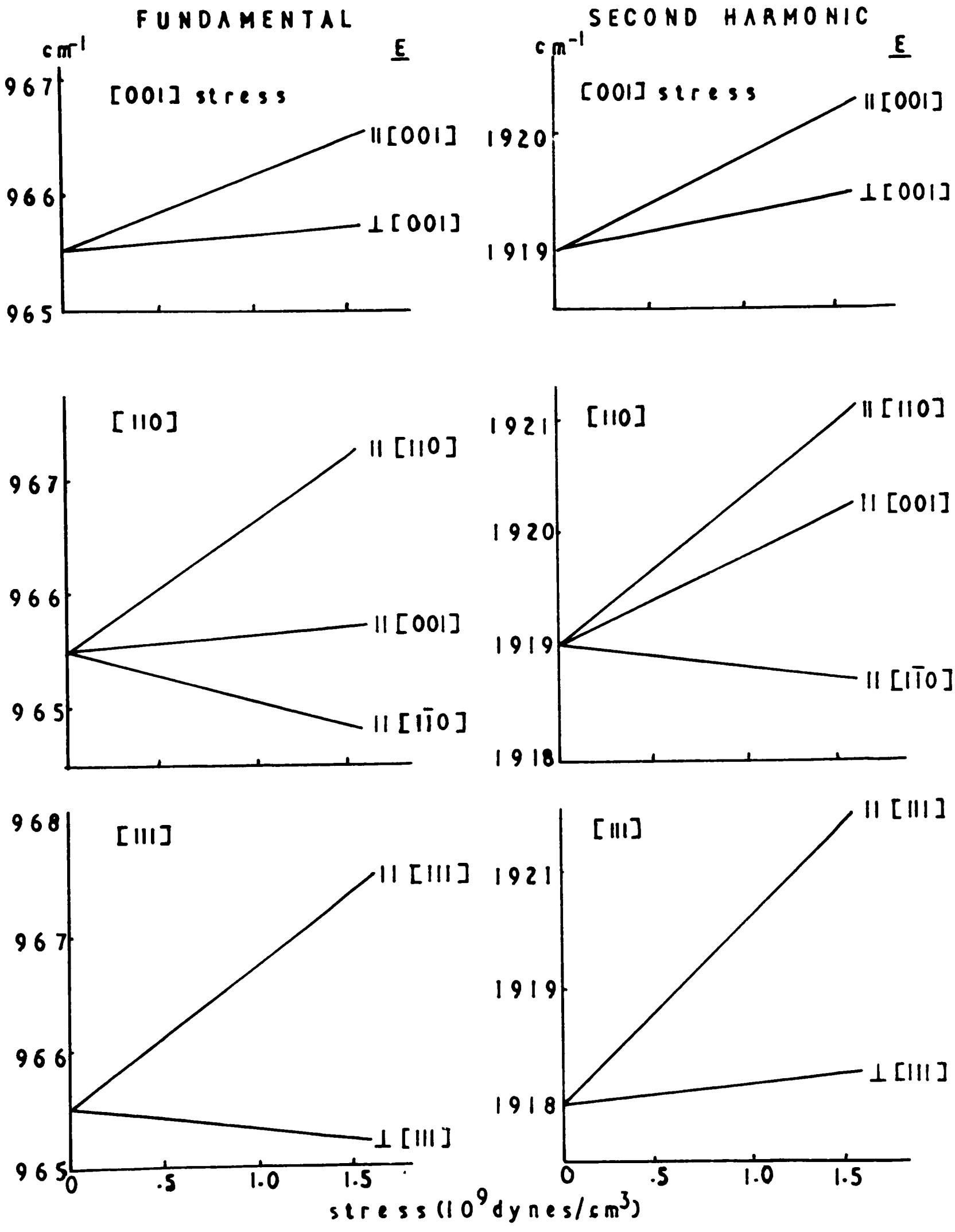
V.1. Introduction

In this chapter, we develop a theory to explain the shift and splitting of localized mode frequencies when the crystal is subjected to applied stress or electric fields. The set of experiments to which the theory will be referred were performed by Hayes and Macdonald (1967) on CaF_2 containing U-centres. This work shows that the fundamental and second harmonic lines are split into two components when stress or an electric field is applied in the (001) or (111) direction and into three components when the direction of the perturbation is (110) (Fig. 1). In the case of applied stress, the first moment of the absorption lines is shifted. All these effects are linear in the applied pressure or electric field.

The experimental results have been fitted to a phenomenological Hamiltonian, derived from symmetry considerations (see e.g. Gebhardt & Maier, 1965), which will in this chapter be derived from a microscopical theory. The defect ion is thought of as vibrating in a potential well created by the force constants coupling it to its neighbours. The potential is given by the tensor equation (see e.g. Maradudin, Montroll & Weiss, 1963)

$$\Phi = \sum_{ij} \Phi^{(2)}_{ij} : \underline{u}_i \underline{u}_j + \sum_{ijk} \Phi^{(3)}_{ijk} : \underline{u}_i \underline{u}_j \underline{u}_k + \cdots \qquad (1)$$

Fig. V.1. Stress splitting of H^- lines
(from Hayes & Macdonald)



where $\underline{u}_i$ is the displacement of the i^{th} ion (defect or neighbour), $\Phi^{(2)}_{ij}$ describes the harmonic coupling between ions i,j, and $\Phi^{(3)}_{ijk}$ and higher coefficients the anharmonic force constants.

Since its mass is considerably less than that of the host atoms, the defect can be thought of as vibrating by itself in a static environment, which in the unstressed crystal gives

$$\Phi = \Phi^{(2)}_{oo} : \underline{u}^2$$

where the anharmonic terms will be neglected. However, when the crystal is stressed and the i^{th} neighbour relaxes a distance $\underline{d}_i$, we can include all the harmonic terms by writing, formally

$$\Phi = \left(\Phi^{(2)}_{oo} + \sum_i \Phi^{(3)}_{ooi} \cdot \underline{d}_i\right) : \underline{u}^2 \qquad (2)$$

where we have put $\underline{u}_i \longrightarrow \underline{u}_i + \underline{d}_i$ for all neighbours in (1) and then considered the harmonic terms in $\underline{u}$, the displacement of the defect itself. (The terms linear in $\underline{u}_i$ always vanish in the internal rearrangements of the crystal which restore equilibrium after applying the external perturbation.) Thus the harmonic part of the potential will be changed by the relaxation of the neighbours, and the vibrational energies will change.

They will also split, in general into three components, because the external perturbation lowers the symmetry of the environment of the defect. Suppose the defect and its environment has symmetry group G before the crystal is stressed. We define a space, Γ, to span all the possible displacements of the defect or its neighbours. Then Γ can be expressed in terms of the irreducible representations $\Gamma_i(G)$ of G :

$$\Gamma = \sum_i a_i \Gamma_i(G)$$

where a_i is an integer coefficient. When a perturbation is applied to the system, the resulting symmetry is S, a subgroup of G. The irreducible representations of S are $\Gamma_i(S)$, which can be used to express $\Gamma_i(G)$:

$$\Gamma_i(G) = \sum_j b_{ij} \Gamma_j(S).$$

Since the strains produced by the perturbation of symmetry S belong to $\Gamma_1(S)$, the identity representation of S, we can say that a strain belonging to $\Gamma_i(G)$ will arise if and only if $b_{i1} \neq 0$ and $a_i \neq 0$.

Applying this consideration to the subgroups of T_d which are produced by various perturbations, we arrive at Table 1 showing the irreducible representations of T_d that will be involved.

Table 1

Perturbation			Representations of T_d containing $\Gamma_1^{(S)}$		
STRESS	0 0 1	D_{2d}	Γ_1	Γ_3	
	1 1 1	C_{3v}	Γ_1		Γ_5
	1 1 0	C_{2v}	Γ_1	Γ_3	Γ_5

We can now construct the phenomenological Hamiltonian by considering the basis functions for these representations that are quadratic in the defect displacement components.

Representation	Basis Functions
Γ_1	$r^2 = x^2 + y^2 + z^2$
Γ_3	$x^2 - y^2$, $r^2 - 3z^2$
Γ_5	xy, yz, zx

Using the symmetrized forms of the elastic constants, S_{ij}, for a cubic crystal, we have for an applied pressure of magnitude F and direction cosines ℓ, m, n

$$\begin{aligned} \mathcal{H} = \{ & B_1 (S_{11} + 2S_{12}) r^2 \\ & + B_3 (S_{11} - S_{12}) [(\ell^2 + m^2 - 2n^2)(r^2 - 3z^2) + 3(\ell^2 - m^2)(x^2 - y^2)] \\ & + B_5 S_{44} [\ell m xy + mn yz + n\ell zx] \} F \end{aligned} \qquad (3)$$

In the case of an applied electric field of magnitude E and direction cosines l, m, n , the perturbation always belongs to Γ_5 of T_d and we have

$$\mathcal{H} = C B'_5 e (lyz + mzx + nxy) \Lambda E , \tag{4}$$

following Hayes and Macdonald (1967), where $\Lambda = \{(n^2+2)/3\}^2$, the Lorentz correction factor, $C = (M\Omega^2)^{-1}$, the inverse of the U-centre mass times its frequency squared, and e is the charge on the U-centre. The B's are parameters which have been fitted to the experimental slopes of the localized mode energies plotted against the applied stress or field. They are, from Hayes and Macdonald

$$B_1 = 5.33 \times 10^4 \text{ erg/cm}^2$$
$$B_3 = 0.59 \times 10^4 \text{ erg/cm}^2$$
$$B_5 = 6.31 \times 10^4 \text{ erg/cm}^2$$
$$B'_5 = 2.1 \times 10^{12} \text{ erg/cm}^2$$

where the last was found assuming e to be one electronic charge.

The number of components into which the external field Hamiltonians above will split the localized mode can be found speedily by the usual group theoretical methods (see e.g. Tinkham, 1964), recognizing that the vibrational mode of the unperturbed U-centre is a p-state.

The above outlines how the phenomenological theory is developed from symmetry considerations and how anharmonicity can account for the magnitude of the shifts. We now proceed to derive the parameters β_i of the phenomenological theory from microscopical ideas. From (2) we see that this requires that we know the displacements, d_i , of the neighbours of the defect and then that we calculate $\mathcal{H}$, the change in the Hamiltonian due to applied stress, which is given by the second term in equation (2). We shall do the latter first, supposing for the time being that we know d_i .

V.2. Anharmonic Force Constants

Because we must write the indices out explicitly, it is convenient to change notation and write $\Phi^{(3)}_{0\alpha i}$, that appears in (2), as $A^i_{\alpha\beta\gamma}$ where α,β,γ are Cartesian indices. Then we can write the second term in (2)

$$\mathcal{H} = \sum A^i_{\alpha\beta\gamma} d^i_\gamma u_\alpha u_\beta \qquad (5)$$

Restricting our attention to the case in which i is a nearest neighbour of the U -centre in CaF_2, we can use symmetry considerations to find the independent components of A . The neighbours of the U-centre are calcium ions, arranged in a tetrahedron around it. If we take

$(=1$ to label the neighbour at (-1, -1, -1), we can find directly the independent components of the bond

$$a \equiv A'_{xxx} = A'_{yyy} = A'_{zzz}$$

$$b \equiv A'_{xxy} = A'_{yyz} = A'_{zzx} = A'_{yyx} = A'_{zzy} = A'_{xxz}$$

$$c \equiv A'_{xyx} = A'_{yzy} = A'_{zxz} = A'_{yxy} = A'_{zyz} = A'_{xzx}$$
$$= A'_{yxx} = A'_{zyy} = A'_{xzz} = A'_{xyy} = A'_{yzz} = A'_{zxx}$$

$$d = A'_{xyz} = A'_{yxz} = A'_{yzx} = A'_{xzy} = A'_{zxy} = A'_{zyx}$$

We can use this simplification due to the symmetry of the problem to rewrite (5) bytransforming the sum over i, δ to a sum over symmetrized coordinates, r .

$$\Phi = \sum A^{i}_{\alpha\beta\gamma} (S^{-1})^{i}_{\gamma r} S_{r\delta}^{j} d^{j}_{\delta} u_\alpha u_\beta$$

$$= \sum A^{(1)}_{\alpha\beta} d^{(1)} u_\alpha u_\beta + \sum \underline{A}^{(3)}_{\alpha\beta} \cdot \underline{d}^{(3)} u_\alpha u_\beta + \sum \underline{A}^{(5)}_{\alpha\beta} \cdot \underline{d}^{(5)} u_\alpha u_\beta .$$

S is the transformation to symmetrized coordinates (see Table IV.1). $A^{(i)}$ and $d^{(i)}$ are respectively the symmetrized forms of A, d, belonging to the representation i, which is either 1, 3 or 5 according to Table 1. $\underline{A}^{(3)}$, $\underline{A}^{(5)}$, $\underline{d}^{(3)}$, $\underline{d}^{(5)}$ have been written as vectors because there is more than one row in these representations, and in the case of 5, two occurrences of the representation.

Using the transformation of Table 1

$$\begin{aligned}\mathcal{H} = {} & \frac{2}{\sqrt{3}}(a+2b)\,r^2 d^{(1)} + \sqrt{\frac{2}{3}}(a-b)(r^2-3z^2)\,d_1^{(3)} - \sqrt{2}\,(a-b)(x^2-y^2)\,d_2^{(3)} \\ & + \sqrt{2}\,c\,(yz\,d_1^{(5)1} + xz\,d_2^{(5)1} + xy\,d_3^{(5)1}) \\ & + 4d\,(yz\,d_1^{(5)2} + xz\,d_2^{(5)2} + xy\,d_3^{(5)2}).\end{aligned} \tag{6}$$

In the case of the shell of second neighbours, which form an octahedron of fluorine ions about the defect, we take $i = 1$ to label the ion at (-1, 0, 0) and, from the operation of the tetrahedral group T_d

$$\begin{aligned} a &\equiv A'_{xxx} \\ b &\equiv A'_{yyx} = A'_{zzx} \\ c &\equiv A'_{yxy} = A'_{zxz} = A'_{xyy} = A'_{xzz} \\ d &\equiv A'_{yzx} = A'_{zyx} \\ e &\equiv A'_{xyz} = A'_{xzy} = A'_{yxz} = A'_{zxy} \end{aligned}$$

with all other elements vanishing. Making the symmetry transformation, we have

$$\begin{aligned}\mathcal{H} = {} & \sqrt{\frac{2}{3}}(a+2b)\,r^2 d^{(1)} + \frac{1}{\sqrt{3}}(a-b)(r^2-3z^2)\,d_1^{(3)} - \sqrt{2}\,(a-b)(x^2-y^2)\,d_2^{(3)} \\ & - 4c(yz\,d_1^{(5)1} + xz\,d_2^{(5)1} + xy\,d_3^{(5)1}) \\ & - 4e(yz\,d_1^{(5)2} + xz\,d_2^{(5)2} + xy\,d_3^{(5)2}) \\ & - 2\sqrt{2}\,d\,(yz\,d_1^{(5)3} + xz\,d_2^{(5)3} + xy\,d_3^{(5)3}).\end{aligned} \tag{7}$$

In equations (6) and (7), the indices on $d^{(i)}$ are self-explanatory. The Cartesians, x, y and z, are the components α, β, γ in (5). There is an obvious surfeit of anharmonic parameters in these

two equations, nine in all, and to give a meaningful fit to the four experimental B'_p of (3), we shall have to make restrictions. This is done later.

V.3. Relaxation Under Stress

Apart from the anharmonic parameters, the unknowns that remain to be found in equations (5) and (6) are the d'_p, the relaxation of the neighbours of the defect when the crystal is subjected to an external field. Here, we consider the case of an applied stress acting on CaF_2 containing U-centres, where the harmonic force constants as well as the mass are changed at the defect. If we were dealing with a perfect crystal, and with only one atom per unit cell, the displacement of each atom would be given directly by the macroscopic elasticity theory. Formally, the displacement

$$\underline{u} = \epsilon . \underline{R}$$

where $\underline{R}$ is the unstrained position of the atom, and the strain tensor

$$\epsilon = S : \sigma$$

Here S is the elastic constant tensor, which is known for CaF_2 (Huffman & Norwood, 1960), and σ, the stress tensor, is given by: is the x component of a force applied to the y component of the crystal surface. In the perfect CaF_2 crystal, this result applies to the relaxation of the Bravais lattice under stress. However, it does not tell us about the rearrangement of the atoms within the unit cell, nor does it tell us about the effect of a defect producing local changes in

the force constants, and destroying the translational symmetry of the crystal. The method that we use for determining the latter will depend on our knowing all the displacements in a perfect CaF_2 lattice under stress, and so we look at this problem first.

V.3.1 Relaxation of Perfect Lattice

The internal strains are in fact easily found, using the long wave method of Born & Huang (1954). Macroscopic elasticity theory is related by them to the microscopic force constants, Φ by expanding the eigenvalue equation in powers of the wavevector up to second order. The internal strain will clearly be given by the displacements due to the optical modes in this limit. The second-order waves which result are just the acoustical waves of the lattice in the limit of long wavelength, and correspond to elastic waves. Before the second order equation is solved, however, the solution of the first-order equation is interpreted by Born & Huang as giving the internal strains. Because CaF_2 has inversion symmetry in the unit cell, it is not piezoelectric, and there is no macroscopic electric field produced by stressing it. Thus Born & Huang's equation (31.34) is equivalent to their (26.18), which they rewrite (26.22)

$$\sum_{\ell K'\beta} \Phi_{\alpha\beta}\left(K K'^{\ell}\right) u_\beta^{(1)}(K') = \sum_{\ell} \Phi_{\alpha\beta}\left(K K'^{\ell}\right) \sum_{\gamma} \epsilon_{\beta\gamma} R_\gamma\left(K K'^{\ell}\right) \quad (8)$$

where the strain tensor, ϵ , and position vector, $\underline{R}\left(K K'^{\ell}\right)$, of the ion in unit cell 0 and site K relative to the ion in cell ℓ

and site K' , have been expressed in our notation. In their equation (26.23), Born & Huang interpret $\underline{u}^{(1)}(K')$ to be the displacement of the K'th ion in any unit cell due to the first-order wave. In (26.24) they point out that this can be assumed to vanish on one of the ions in the unit cell, which we will take to be the calcium ion. Since the second-order equation gives the displacements of the centre of mass of the unit cell, and no other, (8) is clearly the long-wave solution for the optical modes, which we were looking for. We can easily evaluate the left-hand side of (8) in terms of the force constants of the last chapter, and it follows from symmetry that the displacements, $\underline{u}^{(1)}(K')$ of the two fluorines are equal and opposite. The right-hand side is more complicated to deal with, especially as it contains long-range Coulomb contributions, and we rewrite (8), formally

$$(4a+8A+4C)\underline{u} = \{\phi \cdot \epsilon \cdot \underline{R}\} \qquad (9)$$

where the coefficients on the left-hand side are in the notation of section IV.2 and $\underline{u}$ is the displacement of F_2 (see Figure IV.2) which we take to be the sublattice containing the defect. The same result can be obtained by minimising the energy in the unit cell with respect to the displacements of the ions, using our knowledge, from elasticity theory, of the displacements of ions on the same sublattice relative to each other.

We now consider the right-hand side of (9) in terms of shells

of neighbours of the defect, replacing the indices l, K by a notation which describes the individual ions in a given shell of neighbours. The contribution to $\{\phi . \epsilon . \underline{R}\}$ from such a shell is

$$\sum_{B=1}^{n} \phi_{\alpha\beta}^{(B)} \epsilon_{\beta\gamma} R_{\gamma}^{(B)} = \frac{n}{g} \sum_{S=1}^{g} \phi_{\alpha\beta}^{(S)} \epsilon_{\beta\gamma} R_{\gamma}^{(S)}$$

where B labels the bonds from the defect to the n neighbours, and S labels the bonds (not necessarily all different) generated by the g elements of the symmetry group of the shell of neighbours. Now we describe the sum over S in terms of transformation matrices, also called S, which act on ϕ and R :

$$\frac{n}{g} \sum_{S=1}^{g} \phi_{\alpha\beta}^{(S)} \epsilon_{\beta\gamma} R_{\gamma}^{(S)} = \frac{n}{g} \sum_{S} S_{\alpha\lambda} \phi_{\lambda\mu} S_{\mu\beta}^{-1} \epsilon_{\beta\gamma} S_{\gamma\upsilon} R_{\upsilon}$$

$$= \frac{n}{g} \sum_{\beta\gamma} \epsilon_{\beta\gamma} \sum_{\lambda\mu\upsilon} \phi_{\lambda\mu} R_{\upsilon} \sum_{S} S_{\alpha\lambda} S_{\beta\mu} S_{\gamma\upsilon}$$

where in the last expression, we have revoked the Einstein convention and written explicitly the sum over double occurences of the Cartesian indices; we have also made use of the fact that Cartesian coordinates are orthonormal and hence $S^{-1} = S^{T}$.

In the case of a shell of neighbours with tetrahedral symmetry, $S_{\alpha\beta}$ is one of the six 3 x 3 permutation matrices multiplied by one of the four configurations of signs (+ + +), (+ - -), (- + -), (- - +) . Of the $729 = 9^3$ possible $\sum S_{\alpha\lambda} S_{\beta\mu} S_{\gamma\upsilon}$, the only ones that can

be nonzero are the (9 + 9 x 4 x 3 + 9 x 4) sets where $(\alpha,\lambda),(\beta,\mu),(\gamma,\upsilon)$ are either identical pairs or different in both indices. Of these, in fact, the only non-vanishing terms are the 36 where the three pairs are different in both indices, and each of these is 4.

In the case of a shell of neighbours with cubic symmetry, $S_{\alpha\beta}$ is in the above set extended by including inversion. The sum over all S vanishes for all pairs $(\alpha,\lambda),(\beta,\mu),(\gamma,\upsilon)$.

Hence $\{\phi.\epsilon.\underline{R}\}$ has contributions from only these shells of neighbours which have tetrahedral but not cubic symmetry. The contribution from such a shell is the vector

$$\frac{n}{6}\{(\phi_{yz}+\phi_{zy})X+(\phi_{xz}+\phi_{zx})Y+(\phi_{xy}+\phi_{yx})Z\}\begin{pmatrix}\epsilon_{yz}+\epsilon_{zy}\\ \epsilon_{xz}+\epsilon_{zx}\\ \epsilon_{xy}+\epsilon_{yx}\end{pmatrix}. \quad (10)$$

In the case that a shell is beyond the extend of the short-range terms in ϕ (which only go to third neighbours in our treatment), ϕ is the Coulomb interaction alone,

$$\phi_{\alpha\beta}=\frac{Z_d Z_s}{V}\frac{2}{R^3}\left(\delta_{\alpha\beta}-3\frac{R_\alpha R_\beta}{R^2}\right)$$

where the defect and shell have charge Z_d, Z_s , respectively, and are separated by distance $\underline{R}$. The volume, V , is of the unit cell, and in CaF_2

$$Z^2/V = 0.3458 \times 10^4 \text{ dyne/cm}.$$

The Coulomb contribution to $\{\phi \cdot \epsilon \cdot R\}$ is hence

$$-\frac{n}{6}\frac{Z_d Z_s}{v}\frac{18}{R^5} XYZ \begin{pmatrix} \epsilon_{yz}+\epsilon_{zy} \\ \epsilon_{xz}+\epsilon_{zx} \\ \epsilon_{xy}+\epsilon_{yx} \end{pmatrix} \qquad (11)$$

The reason this expression does not diverge when summed across the whole crystal is that it alternates in sign, owing to the alternate orientations, as it were, of the tetrahedra.

The coefficients in (10) and (11) must now be summed over the lattice. In spite of the alternation in sign, the convergence of (11) as we proceed to shells of neighbours at greater distances from the defect is rather slow, and we content ourselves with going out to the eleventh term of $\{\phi \cdot \epsilon \cdot \underline{R}\}$, whose contribution is 1% of the coefficient on the left-hand side of (9), $4a + 8A + 4C = -11.622 \times 10^4$ dyne/cm . We obtain for the displacement due to internal strain of the sublattice on which the defect is situated in the perfect crystal

$$\underline{u} = \eta_k r_0 \begin{pmatrix} \epsilon_{yz}+\epsilon_{zy} \\ \epsilon_{xz}+\epsilon_{zx} \\ \epsilon_{xy}+\epsilon_{yx} \end{pmatrix}$$

where the coefficient η_k comes from the sum we have just performed and is

$$\eta_k = -0.063$$

If the applied uniaxial pressure, F, has direction cosines l, m, n,

$$\epsilon = S:\sigma = \begin{pmatrix} l^2 S_{11} + (m^2+n^2) S_{12} & lm\, S_{44} & ln\, S_{44} \\ lm\, S_{44} & m^2 S_{11} + (l^2+n^2) S_{12} & mn\, S_{44} \\ ln\, S_{44} & mn\, S_{44} & n^2 S_{11} + (l^2+m^2) S_{12} \end{pmatrix} F.$$

Hence

$$\begin{pmatrix} \epsilon_{yz} + \epsilon_{zy} \\ \epsilon_{xz} + \epsilon_{zx} \\ \epsilon_{xy} + \epsilon_{yx} \end{pmatrix} = 2F S_{44} \begin{pmatrix} mn \\ ln \\ lm \end{pmatrix}$$

and the other elastic displacements, $u = \epsilon \cdot R$ in the perfect lattice can be found. For instance, the displacement of the nearest neighbour calcium at $(-1\ -1\ -1)\, r_0/2$ is

$$-\begin{pmatrix} l^2 S_{11} + (m^2+n^2) S_{12} + (lm+ln) S_{44} \\ m^2 S_{11} + (l^2+n^2) S_{12} + (lm+mn) S_{44} \\ n^2 S_{11} + (l^2+m^2) S_{12} + (ln+mn) S_{44} \end{pmatrix} F \frac{r_0}{2}$$

and of the second neighbour fluorine at $(1\ 0\ 0)$ is

$$\begin{pmatrix} l^2 S_{11} + (m^2+n^2) S_{12} \\ lm\, S_{44} \\ ln\, S_{44} \end{pmatrix} F r_0 - 2k\, S_{44} \begin{pmatrix} mn \\ ln \\ lm \end{pmatrix} F r_0 .$$

S is, of course, the elastic constant tensor, in Voigt notation, and the components given are the only non-zero ones in a crystal of cubic symmetry.

We shall need the above displacements in symmetrized form, and so we use S of TableIV.1to make the transformation to $S\cdot\underline{u}$, where $\underline{u}$ is the vector consisting of all displacements, constructed like the above, for each ion in the shells of first and second neighbours. Doing this, we have for $S\underline{u}/Fr_0$

$$\begin{aligned}
\Gamma_1 \quad & -\tfrac{1}{\sqrt{3}}\left(S_{11}+2S_{12}\right)\left(\tfrac{1}{\sqrt{2}}\right) \\
\Gamma_3 \quad & -\tfrac{1}{\sqrt{6}}\left(S_{11}-S_{12}\right)\left(\ell^2+m^2-2n^2\right)\left(\tfrac{1}{\sqrt{2}}\right) \\
& -\sqrt{\tfrac{3}{2}}\left(S_{11}-S_{12}\right)\left(\ell^2-m^2\right)\left(\tfrac{1}{\sqrt{2}}\right) \\
\Gamma_5 \quad & S_{44}\,mn\begin{pmatrix} 2k \\ -\sqrt{2} \\ 0 \\ 2 \\ -4k \\ -2\sqrt{2}k \end{pmatrix} \qquad (12)
\end{aligned}$$

second row ℓn third row ℓm

V.3.2 Relaxation of Imperfect Lattice

In the imperfect lattice, the translational symmetry of the force constants is destroyed, and the whole crystal becomes a single unit cell. The methods of the previous section no longer work. However, the previous section has given us the results for the perfect lattice, and we can try comparing the imperfect lattice with this.

Since the energy of any crystal in the harmonic approximation is, formally

$$V = \frac{1}{2} \Phi : \underline{u}\,\underline{u}$$

we can write the force due to a displacement $\underline{u}$

$$-F = \frac{\partial V}{\partial \underline{u}} = \Phi \cdot \underline{u} \qquad (13)$$

In these equations, the vectors $\underline{F}, \underline{u}$ have components at each of the ions in the crystal, and the matrix Φ couples all these components. Equation (13) gives the displacement, $\underline{u}$, of all the ions due to an applied force, F, if the ions are coupled by force constant matrix, Φ. If we now restrict our notation and consider (13) to refer to the perfect lattice, we can write an equivalent equation for the imperfect lattice

$$-F = (\Phi + \varphi) \cdot \underline{w} \qquad (14)$$

where φ gives the change in the force constants and $\underline{w}$ the new displacements, which arise in the imperfect lattice due to F. The important consideration is that F is the same here and in (13), so that the right-hand sides of the two equations can be identified. F is a vector independent of the crystal, apart from the surface, arising from the external applied force only, and is nonzero only at the surface of the crystal. Making the identification of (13) and (14),

$$\underline{w} = (\phi+\varphi)^{-1}\phi\cdot\underline{u} = (1+\phi^{-1}\varphi)^{-1}\cdot\underline{u} \equiv (1+g\varphi)^{-1}\cdot\underline{u} \qquad (15)$$

Equation (15) gives us a formal solution of the imperfect lattice relaxation in terms of the relaxation of the perfect lattice. The reason it is useful is that φ is a small matrix, extending only over the size of the defect. Thus we need only a small number of components of $\underline{u}$, and if we restrict the number of components of $\underline{w}$ with which we will be satisfied, we need to know g only over the extent of the defect as well. This means that in the case of CaF_2 with a defect extending to second neighbours, (15) is a 33 x 33 equation. It can be further simplified by the symmetry considerations of Section IV.2..

Before we go on to apply (15) to calcium fluoride, it is instructive to examine its application to a simpler case. We consider the nearest-neighbour linear chain with a single force constant defect, k', where the normal force constant is k. Thus $\varphi = k'-k \equiv \delta k$ where $\delta \equiv (k'-k)/k$. In this case g is, according to Chapter I

$$g(x,x') = \frac{1}{Nk}\sum \frac{e^{iq(x-x')}}{\sum_{i=0,nn}(1-e^{iqx_i})}$$

where the denominator is summed over the two neighbours of a site and the site itself, and is the eigenvalue, $(\omega)^2_q$, for the vibratio problem of the linear chain. The following simple relations can be seen to hold, where $Z=2$ is the number of nearest neighbours, and a

is the distance between neighbours,

$$g(a) = -\frac{1}{kz} + g(0)$$

$$\sum_{i=n.n.} g(x,x_i) = -\frac{\delta(x)}{k} + z\,g(x).$$

An easy approach to the problem is to find V, where $W = u + V$, using an equivalent of (15)

$$v = -g\varphi(u+v).$$

Then for the ℓ^{th} mass to the right of the defect

$$v(\ell a) = V(a) = -\frac{\delta}{1+\delta}\,\epsilon a,$$

where ϵ is the elastic strain tensor. From symmetry,

$$v(-\ell a) = v(-a) = -v(a).$$

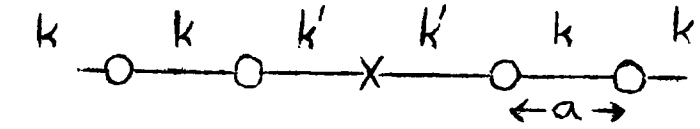
The multiplier of ϵa contains all the k'-dependence of the relaxation, and is plotted in Figure 2. We note its resemblance to the equivalent of (15),

$$V = -\frac{g\varphi}{1+g\varphi}\,u$$

the general form. This is also plotted in the case of a one-dimensional representation, and we see the general features of the relaxation, W. V goes to -1, so that W goes to 0, when φ becomes large and the neighbours more and more rigidly bound to the defect. When φ decreases,

Fig V·2

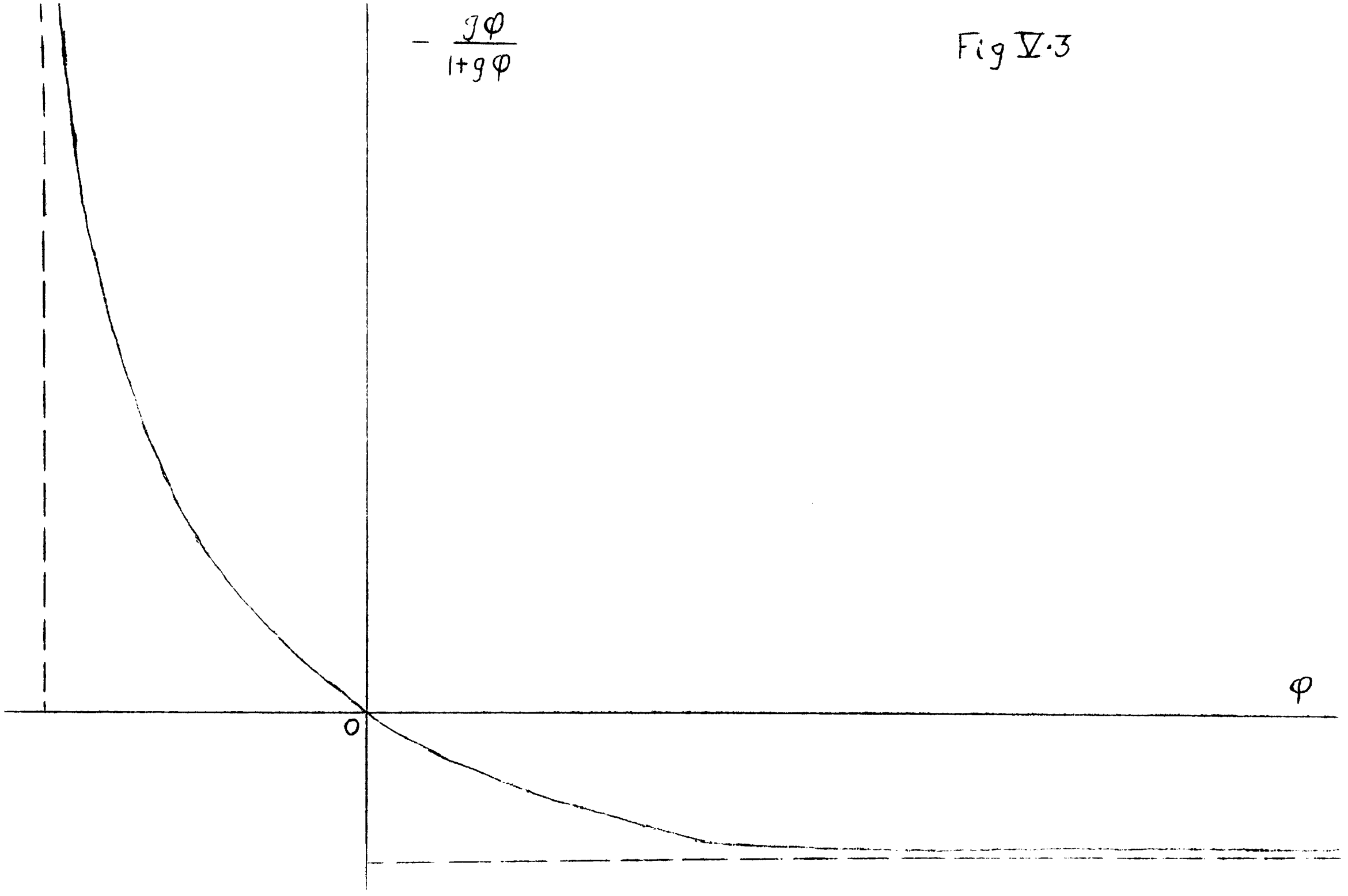
LINEAR CHAIN



$$\delta = \frac{k'-k}{k}$$

$$-\frac{J\varphi}{1+g\varphi}$$

Fig V·3



the relaxation becomes that of the perfect lattice at $\varphi = 0$, and then increases to infinity at the point where φ is sufficiently replusvie to destroy the resistance of the lattice to this type of motion. We return to calcium fluoride.

The symmetrized form of w, in (15), are directly the d's in (6) and (7) that we are looking for. They are obtained for each representation, Γ_i , by writing in (15) the U's from (12) and g's and φ's from sect. IV.2. If we restrict the anharmonic force constants in (6) and (7) to central forces only (i.e. to forces depending only on the magnitude, $|R|$, of the separation between neighbours), distinguish first and second neighbours by subscripts 1 and 2 on the force constants, and split the Hamiltonian into three parts of different symmetry

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_3 + \mathcal{H}_5$$

and (6) and (7) become:

$$\mathcal{H}_1 = -\tfrac{2}{3} r_0 (S_{11}+2S_{12}) [3a_1, \tfrac{1}{\sqrt{2}}(a_2+2b_2)] \left[\frac{1}{1+g\varphi}\right]_1 \left[\begin{matrix}1\\ \sqrt{2}\end{matrix}\right] r^2 F$$

$$\mathcal{H}_3 = -\tfrac{1}{3} r_0 (S_{11}-S_{12}) [0, \tfrac{1}{\sqrt{2}}(a_2-b_2)] \left[\frac{1}{1+g\varphi}\right]_3 \left[\begin{matrix}1\\ \sqrt{2}\end{matrix}\right] (l^2+m^2-2n^2)(r^2-3z^2) F$$

$$\mathcal{H}_5 = r_0 S_{44} [-8c_1, 4\sqrt{2}c_1, 4c_1, 0, 0, 0] \left[\frac{1}{1+g\varphi}\right]_5 \begin{bmatrix} 1 \\ -\frac{1}{\sqrt{2}} \\ 0 \\ 1 \\ -2 \\ -\sqrt{2} \end{bmatrix} (lmxy+mnyz+nlzx) F \qquad (19)$$

The results of calculating these terms will be discussed after considering relaxation when the external perturbation is an electrical field.

V.4. Relaxation under Electric Field

In this section, we find a Hamiltonian similar to (19) for an imperfect lattice in an external electric field. Again, the method is to find the relaxation in the imperfect lattice in terms of that in the perfect lattice. Equation (13) becomes

$$-Z\underline{E} = \Phi \cdot \underline{u} \tag{20}$$

and (14)

$$-(Z+\Delta Z)\underline{E} = (\Phi+\varphi)\cdot \underline{w}$$

where Z represents the charges on the ions, and ΔZ the change in charge at the defect site. We note that in this case it is no longer the force but the electric field which remains the same in perfect and imperfect lattices. Hence

$$\underline{w} = (\Phi+\varphi)^{-1}[\Phi\cdot\underline{u} + \Delta Z\underline{E}] = \frac{1}{1+g\varphi}[\underline{u} + g\cdot\Delta Z\underline{E}] \tag{21}$$

Here again, the result may be restricted to a space the size of the defect, and then further simplified by symmetry consdierations.

In the perfect lattice, the problem reduces to the size of the unit cell, for the ions on any sublattice all have the same charge, and the sublattice moves rigidly under an electric field. Inserting in (20) the labels, ℓ , of the unit cell

$$-Z_{\ell\ell'}\underline{E} = \sum_{\ell'} \Phi_{\ell\ell'}\underline{u}_{\ell'}$$

where E is independent of ℓ, and Z is a diagonal matrix of charges on each ion. By the argument of the first sentence of this paragraph, u is also independent of ℓ', and, by translational symmetry, so is Φ. Thus we can replace the sum over ℓ' by a factor N. Finally we sum over ℓ.

$$-NZ\underline{E} = N\sum_{\ell} \Phi_{\ell} \cdot \underline{u} = N\, D(\underline{q}=0)$$

where $D(\underline{q})$ is the dynamical matrix of section I.2. Cancelling the factors of N, we are left with a 3 x 3 equation, since the 9 x 9 $D(\underline{q}=0)$ is composed of diagonal 3 x 3 blocks.

$$-\begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix} Z\underline{E} = \begin{pmatrix} -8a & 4a & 4a \\ 4a & -4a-4A-2C & 4A+2C \\ 4a & 4A+2C & -4a-4A-2C \end{pmatrix} \begin{pmatrix} \underline{u}_{Ca} \\ \underline{u}_{F_1} \\ \underline{u}_{F_2} \end{pmatrix}$$

where $z = 0.7789e$ is the number of electronic charges on the fluorine ions, and the other coefficients are force constants defined in section IV.2. The matrix is singular, but we obtain two relationships from it

$$\underline{u}_{F_2} = \underline{u}_{F_1}$$

$$2\underline{u}_{Ca} - \underline{u}_{F_1} - \underline{u}_{F_2} = \frac{1}{2a} Z\underline{E} ,$$

which give us

$$\underline{u}_{F_2} = -\frac{1}{4a} Z\underline{E} \qquad (22)$$

if we suppose $\underline{U}_{Ga} = 0$. This is an assumption equivalent to supposing that the centre of mass of the crystal does not move, valid for a neutral crystal, since the problem is not affected by translations of the crystal as a whole.

Using (22) for $\underline{U}$ in (21), and writing the $\underline{w}$ obtained in symmetrized form, it becomes, as in the stress case, the $\underline{d}$ required in (6) and (7). As anticipated in sect. 1, only those $\underline{d}'s$ appear, in the electric field case, which belong to Γ_5 . We have an electric field Hamiltonian

$$\mathcal{H}_5 = \Lambda\,[-8c_1,\ 4\sqrt{2}\,c_1,\ 4c_1,0,0,0]\left[\frac{1}{1+9\varphi}\right]_5 \left\{ -\frac{z}{4a}\begin{bmatrix}1\\0\\0\\0\\2\\\sqrt{2}\end{bmatrix} + g_{\Delta 0}\Delta z \right\} \times$$

$$\times (E_x yz + E_y zx + E_z xy) \qquad (23)$$

which is to be compared with (4). The Lorentz factor, Λ , enters because the electric field $\underline{E}$ in (20) is that experienced by the ions within the crystal. The anharmonic force constants appearing in (23) are those of $\mathcal{H}_5$ in (19). The indices Δ and 0 on g mean that we consider these elements of g between the neighbours, Δ , (in symmetrized coordinates) and the defect itself, 0.

V.5. Results

We now perform the calculation of the coefficients in (19) and (23), and compare with (3) and (4). Before we do this, however, we must decide on a value for Δz , for (23) depends on this

explicitly, and also φ depends on ΔZ, as pointed out in section IV.3. It is seen that the last equation in (19) is in the one parameter, C_1, as is (23). That these should give the same result for C_1, is a criterion for finding ΔZ. The fact, however, that they are the same equation leaves us with only three independent equations in (19) and (23), and means that we cannot fit four anharmonic parameters.

It is relevant to consider the analytic form of an anharmonic central force potential before progressing further, for we will obtain further relationships among the force constants. A potential $\varphi(r)$ which in fact depends only on the modulus of $\underline{r}$, r, can be Taylor expanded about small displacements, $\underline{u}$, in the direction of $\underline{r}$, to give

$$\varphi(|\underline{r}+\underline{u}|) = \varphi(r) + \tfrac{1}{2}(\underline{u}\cdot\underline{r})^2 g(r) + \tfrac{1}{6}\left\{2(\underline{u}\cdot\underline{u})(\underline{u}\cdot\underline{r})\, g(r) + (\underline{u}\cdot\underline{r})^3 \tfrac{1}{r} g'(r)\right\} + \cdots$$

where

$$g(r) = \frac{1}{r}\frac{\partial}{\partial r}\left[\frac{1}{r}\varphi'(r)\right]$$

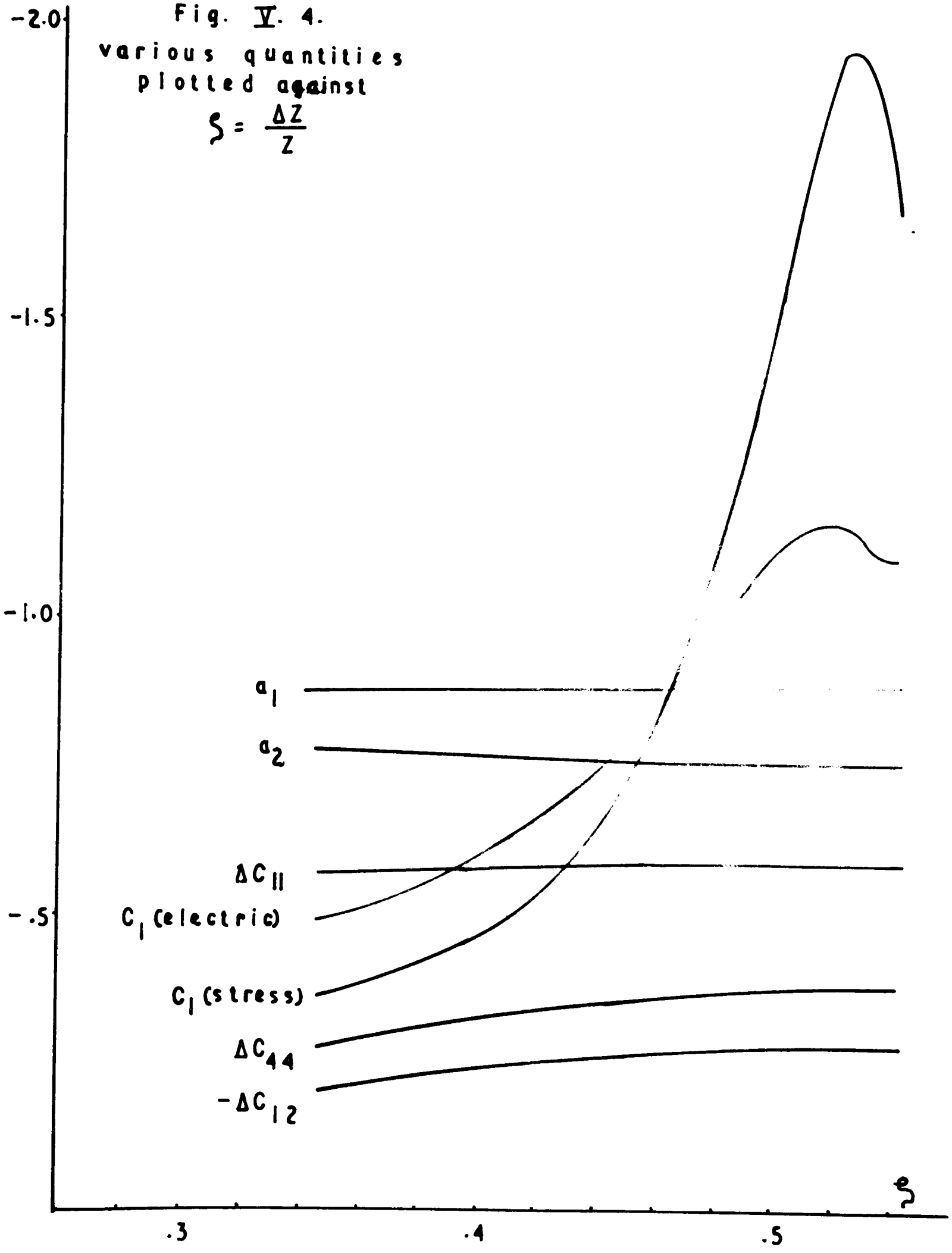
and the coefficient of the term linear in $\underline{u}$ vanishes for static equilibrium.

Thus we have a single harmonic central term, and two anharmonic central terms, in agreement with above. However, one of the anharmonic terms is given by the same function as the harmonic, and for our case we can write

Fig. V. 4.

various quantities plotted against

$$\zeta = \frac{\Delta Z}{Z}$$



$$\text{(a) HARMONIC CENTRAL n.n.} = \frac{r_0^2}{8} g(r_{n.n.})$$

$$\text{(b) HARMONIC CENTRAL 2n.n.} = \frac{r_0^2}{2} g(r_{2n.n})$$

$$\text{(c)} \qquad a_1 - c_1 = \frac{r_0}{24} g(r_{n.n.})$$

$$\text{(d)} \qquad a_2 - b_2 = \frac{r_0}{3} g(r_{2n.n.}) \qquad (24)$$

$$\text{(e)} \qquad c_1 = \frac{r_0^3}{48} \frac{g'(r_{n.n})}{r_{n.n.}}$$

$$\text{(f)} \qquad b_2 = \frac{r_0^3}{6} \frac{g'(r_{2n.n.})}{r_{2n.n.}}$$

where r_0 is the lattice parameter and $r_{n.n.} = \frac{\sqrt{3}}{2} r_0$, $r_{2n.n.} = r_0$.

Agreement between the first and second pairs of these equations can be taken as a second criterion for finding ΔZ . As it happens, these two conditions do not give exactly the same result for ΔZ , (see Figure 4), which is not very surprizing, considering the inaccuracy inherent in our method of dealing with changed charge on the defect. Therefore, the method we follow is to use (19) to determine a_1 and, from this (24) to determine c_1, in the nearest neighbour case. Then (23) or the third equation of (19) gives ΔZ . Since (19) gives the results for a_1 which are essentially independent of ΔZ , we avoid the inaccuracies of our restricted method by finding the anharmonic force constants in this way. The results are:

$$a_1 = -.887 \times 10^{12} \text{ dyne/cm}^2 \quad (-.773 \times 10^{12} \text{ dyne/cm}^2)$$
$$c_1 = -.798 \times 10^{12} \text{ dyne/cm}^2 \quad (-.330 \times 10^{12} \text{ dyne/cm}^2)$$

$$\zeta \equiv \frac{\Delta z}{z} = \begin{cases} -0.458 & \text{(from (23))} \quad \text{ELECTRIC} \\ -0.452 & \text{(from (19))} \quad \text{STRESS} \end{cases}$$

The figures in parenthesis give the results if φ had been taken to equal zero in (19), i.e. if the strain had caused only perfect lattice type relaxation near the defect. In this case, as c_1 is also clearly independent of Δz, its value has been obtained directly from (19). This compares with the value $-.458 \times 10^{12}$ dyne/cm^2 obtained for the $\varphi = 0$ case from (23), but not with the value $-.684 \times 10^{12}$ dyne/cm^2 obtained in this case from (24) using $a_1 = -.773 \times 10^{12}$ dyne/cm^2,

The value of ζ above should be compared with $\zeta = -.467$ obtained from the condtion that (19c) and (23) give the same result for c_1. These values of ζ give for the changes in the central harmonic force constants, respectively:

n.n.	- 65%	- 66%
2n.n.	- 22 %	- 21%

For second neighbours, the second equation of (19) and the fourth of (24) are similar, and worked out independently give

$$a_2 - b_2 = -.760 \times 10^{12} \text{ dyne/cm}^2 \quad (-.640 \times 10^{12} \text{ dyne/cm}^2)$$
and $$a_2 - b_2 = -.694 \times 10^{12} \text{ dyne/cm}^2$$

respectively, where the second result was obtained by using (24b) to get $g(r_{2n.n})$ from the harmonic central second neighbour force. The agreement is reasonable, considering that the harmonic forces used are not purely central, but have noncentral components as well. Once again, however, the identity of the two equations in the second neighbour harmonic forces reduces the number of independent parameters we can hope to find, and we have to make an arbitrary assignment, $b_2 = 0$. This was done above to find the nearest-neighbour force constant a_1.

The results for the nearest-neighbour case may be compared to a potential whose r-dependence is known, and the last two equations of (24) can thus be related to the previous ones. We try a Lennard-Jones potential (which includes van der Waals and repulsive terms).

$$\varphi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

for which

$$g(r) = 4\epsilon\,\frac{6\times4}{\sigma^4}\left(\frac{\sigma}{r}\right)^{10}\left[7\left(\frac{\sigma}{r}\right)^{6} - 2\right]$$

and

$$g'(r) = -4\epsilon\,\frac{6\times4\times4}{\sigma^5}\left(\frac{\sigma}{r}\right)^{11}\left[28\left(\frac{\sigma}{r}\right)^{6} - 5\right].$$

The parameters ϵ, σ can be found from $g_1 = g\left(\frac{\sqrt{3}\,r_0}{2}\right)$ and $g_2 = g(r_3)$ in (24):

$$\left(\frac{\sigma}{r_1}\right)^6 = \frac{2}{7}\,\frac{1 - \left(\frac{\sqrt{3}}{2}\right)^{10}\frac{g_1}{g_2}}{1 - \left(\frac{\sqrt{3}}{2}\right)^{16}\frac{g_1}{g_2}}$$

$$g_1 = -.787 \times 10^{20} \text{ dyne/cm}^3$$
$$g_2 = -.644 \times 10^{20} \text{ dyne/cm}^3$$

from the equations of (24) involving the harmonic force constants.

Thus

$$\frac{r}{\sigma} = 1.28$$

$$\epsilon = 2.04 \times 10^{-12} \text{ erg.}$$

Using these values, we can calculate

$$g_1' \equiv g'\left(\frac{\sqrt{3}\, r_0}{2}\right) = -3.55 \times 10^{28} \text{ dyne/cm}^4$$

which is compared with

$$g'_1 = -4.47 \times 10^{28} \text{ dyne/cm}^4 \quad (-1.85 \times 10^{28} \text{ dyne/cm}^4)$$

obtained by using the calculated value of c_1 in (24 f).

The minimum of the Lennard-Jones potential is at $r/\sigma = 1.12$ and the nearest-neighbour distance, r/σ in the inert-gas solids, for which this potential is most applicable, is within a few per cent of this value. (see e.g. Kittel, 1966). In view of this, the value $r/\sigma = 1.28$ is rather large. However, it must be remembered that r in this case is the nearest neighbour separation in the perfect lattice. When a hydrogen or deuterium ion is substituted for one of the host fluorines, the lattice relaxes around the smaller defect (an effect which in our consideration hitherto has been equivalent to a change in the force constants), thus reducing the

effective r_1 . The energy $\epsilon = 2.04 \times 10^{-12}$ erg is of the correct order of magnitude for an ionic crystal, and we conclude that for nearest neighbours of the U-centre, a Lennard-Jones potential provides the approximate amount of first-order anharmonicity to account for the splitting under stress and electric field of the localized mode.

CHAPTER VI

ELASTIC CONSTANTS OF AN IMPERFECT CRYSTAL

Because the elastic constants can be derived directly from the force constant matrix by the long wave method (Born & Huang, 1954), it is a tempting error to suppose that the elastic constants of an imperfect crystal are found from a configuration average of the imperfect force constants (see e.g. Liu & Shimizu, 1967). This approach, however, gives a result which disagrees with that given by the slope of the generalized dispersion relation for phonons in the imperfect lattice. (Benedek & Nardelli, 1967). In that case, the dispersion relation is, to first order in , the defect concentration,

$$\tilde{\omega}^2_{\underline{q}j} = \omega^2_{\underline{q}j} - c\langle\langle \underline{q}j | T | \underline{q}j \rangle \qquad (1)$$

where $\underline{q}$ and j are the phonon wave vector and branch index, respectively; $\tilde{\omega}_{\underline{q}j}$ and $\omega_{\underline{q}j}$ are the perturbed and host lattice frequencies; T is the T-matrix for a single defect.

The present chapter develops an approach which leads to the same result as given by the dispersion relation above. The essential innovation is that the effect of the altered strains in an imperfect crystal is included in the configuration average. As before, we consider that the force applied to the crystal is an external variable, independent

of the configuration of defects. Thus, for a given configuration, we have, formally,

$$-F = (\phi + \varphi) w \qquad (V.13)$$

where φ is the change in the force constant matrix ϕ produced by the configuration of defects; w is the displacement of the atoms in the crystal due to F, the applied force. Taking the average over all configurations,

$$-F = \langle (\phi + \varphi) w \rangle$$

where we are not entitled to take w out of the average, because it depends on the proximity of a defect. In order to do the long wave method on a force constant matrix, however, it is necessary to separate the force constants from the displacements, and so this is done by introducing an effective potential, $\phi + \delta\phi$, satisfying

$$-F = (\phi + \delta\phi) \langle w \rangle. \qquad (2)$$

Comparing these two,

$$\delta\phi \langle w \rangle = \langle \varphi w \rangle. \qquad (3)$$

Now we know that

$$w = \frac{1}{1+g\varphi} u = (1+gT) u \qquad (V.15)$$

where

$$T = \frac{-\varphi}{1+g\varphi} \tag{4}$$

and

$$g = \phi^{-1}.$$

Hence

$$\langle w \rangle = (1+g\langle T\rangle)u$$

and

$$\langle \varphi w \rangle = \langle \varphi + \varphi g T \rangle u = -\langle T \rangle u$$

where g, u are quantities referring to the perfect lattice, and so can be taken outside the configuration average, Thus, from (3),

$$\delta\phi(1+g\langle T\rangle)u = -\langle T\rangle u .$$

The vector u can be removed from both sides of this equation if all its components can be considered independent. While this is not the case in the applications we deal with, it is easy to conceive a situation, in principle, in which the displacements of all the atoms are independent of each other, and so we can write

$$\delta\phi = -\langle T\rangle(1+g\langle T\rangle)^{-1} \tag{5}$$

In finding the configuration average $\langle T \rangle$, we note first that for a given configuration, $\varphi = \sum_i \varphi_i$, where each φ_i is the change in force constants due to a single defect, i. To first order in concentration of defects, C, (4) can be written

$$T = \frac{-\Sigma \varphi_i}{1+g\Sigma\varphi_i} \simeq \sum_i \frac{-\varphi_i}{1+g\varphi_i} = \sum_i T_i \qquad (6)$$

where T_i is the T-matrix for the single defect, i.

This step is seen to be valid on expanding the left hand side

$$\frac{-\Sigma\varphi_i}{1+g\Sigma\varphi_i} = -\sum_i \varphi_i \left[1 - g\sum_j \varphi_j + g\sum_j \varphi_j g\sum_k \varphi_k - \cdots\right]$$

$$= -\sum_{ijk\cdots} \varphi_i \left[1 - g\varphi_j + g\varphi_j g\varphi_k - \cdots\right]$$

$$= -\sum_i \varphi_i \left[1 - g\varphi_i + g\varphi_i g\varphi_i - \cdots\right]$$

$$-\sum_{ijk\cdots}{}' \varphi_i \left[-g\varphi_j + g\varphi_j g\varphi_k - \cdots\right],$$

where the prime on the final sum means that the indices $j, k, \cdots$ are never allowed to equal i. It is seen that the first term of the final expression, involving only the defect i, is equal to the right hand side of (6). The second term does not contribute to the first order in concentration, C, because it involves products of at least two non-identical defect sites, and when it is averaged over all

configurations of defects, these give terms of at least second order in c. For a similar reason, the first term contains only terms that are linear in C.

So far, we have made no assumptions about the extent or similarity of the defects, $($. Now we suppose that all the defects are of the same type, and write (6)

$$T = \sum T_i = \begin{pmatrix} \ddots & & & \\ & T_0 & & \\ & & T_0 & \\ & & & T_0 \ddots \end{pmatrix}$$

where the T_0 are small block matrices, distributed along the diagonal according to the configuration of defects. Elsewhere, T is zero. We now take a configuration average, and have

$$\langle T \rangle = c T_0 \begin{pmatrix} 1 & & \\ & 1 & \\ & & \ddots \end{pmatrix} = c T_0 \times I$$

where the 1's are block unit matrices, everywhere on the diagonal. Thus we have for (5)

$$\delta\Phi = \frac{-cT_0 \times I}{1 + gcT_0 \times I} \simeq -cT_0 \times I \qquad (7)$$

where the second equation is a restriction to first order in the

concentration. T_0 is just the T-matrix for a single defect, and so we finally have for (2)

$$-F = (\Phi - c T_0 \times I) \langle w \rangle$$

It only remains to do the long wave method on $\Phi - cT$, and we have the same results for the elastic constants as given by (1).

For comparison, the derivation of (1) is briefly sketched, following Langer (1961), Taylor (1964) and Izyumov (1966).

In the three dimensional Bravais lattice with mass and force constant changes on the defects,

$$\Delta_{\alpha\beta}^{\ell\ell'} = \delta_{\ell\ell'}\delta_{\alpha\beta}\epsilon_\ell M\omega^2 - \varphi_{\alpha\beta}(\ell,\ell'),$$

we have the phonon equation of motion (Maradudin, Montroll & Weiss, 1963)

$$M\omega^2 u_\alpha(\ell) - \sum_{\beta\ell} \Phi_{\alpha\beta}(\ell\ell') u_\beta(\ell') = \sum_{\beta\ell'} \Delta_{\alpha\beta}^{\ell\ell'} u_\beta(\ell')$$

where M is the mass of the atoms of the host lattice, m_ℓ that of the atom at site ℓ, $\epsilon_\ell = (M - m_\ell)/M$, Φ is the perfect lattice force constant matrix, φ the change in force constants induced by the defect, ℓ and ℓ' site labels, and α and β Cartesian labels. This equation is diagonalized by Fourier transforming

$$u_\alpha(\ell) = \frac{1}{\sqrt{NM}} \sum_{\underline{q}j} e_\alpha\left(\frac{q}{j}\right) Q\left(\frac{q}{j}\right) e^{2\pi i \underline{q}\cdot\underline{x}(\ell)}$$

where q, j are the phonon and branch labels, Q is the normal coordinate, and e the polarization vector. N is the number of unit cells. We now restrict our attention to the linear chain with mass defect for simplicity of notation, and follow Langer (1961). The result of Fourier transforming is

$$(\omega^2-\omega_q^2)\, Q_q = \sum V_{qq'} Q_{q'}$$

$$V_{qq'} = \frac{\omega_{q'}^2}{N} \sum_{\ell} \frac{\epsilon_\ell}{1-\epsilon_\ell}\, e^{2\pi i (q'-q)\ell}$$

where ω_q is the eigenfrequency of the perfect lattice.

Langer now defines the phonon propagator, G, for the imperfect lattice by

$$[G^{-1}(\omega^2)]_{qq'} = (\omega^2-\omega_q^2)\,\delta_{qq'} - V_{qq'}.$$

It follows that

$$G_{qq'}(\omega^2) = \frac{\delta_{qq'}}{\omega^2-\omega_q^2} + \frac{1}{\omega^2-\omega_q^2} \sum_{q''} V_{qq''}\, G_{q''q'}(\omega^2).$$

This may be iterated:

$$G_{qq'}(\omega^2) = \frac{\delta_{qq'}}{\omega^2-\omega_q^2} + \frac{1}{\omega^2-\omega_q^2} V_{qq'} \frac{1}{\omega^2-\omega_{q'}^2} + \frac{1}{\omega^2-\omega_q^2} \sum_{q_1} \frac{V_{qq_1} V_{q_1 q'}}{\omega^2-\omega_{q_1}^2} \frac{1}{\omega^2-\omega_{q'}^2} + \cdots$$

$$= g_q \delta_{qq'} + g_q V_{qq'} g_{q'} + \sum_{q_1} g_q V_{qq_1} g_{q_1} V_{q_1 q'} g_{q'}$$

where the propagator for the perfect lattice, g, has been introduced:

it is diagonal in q because of translational symmetry. To restore translational symmetry in the imperfect lattice, a configuration average is taken, and Langer has

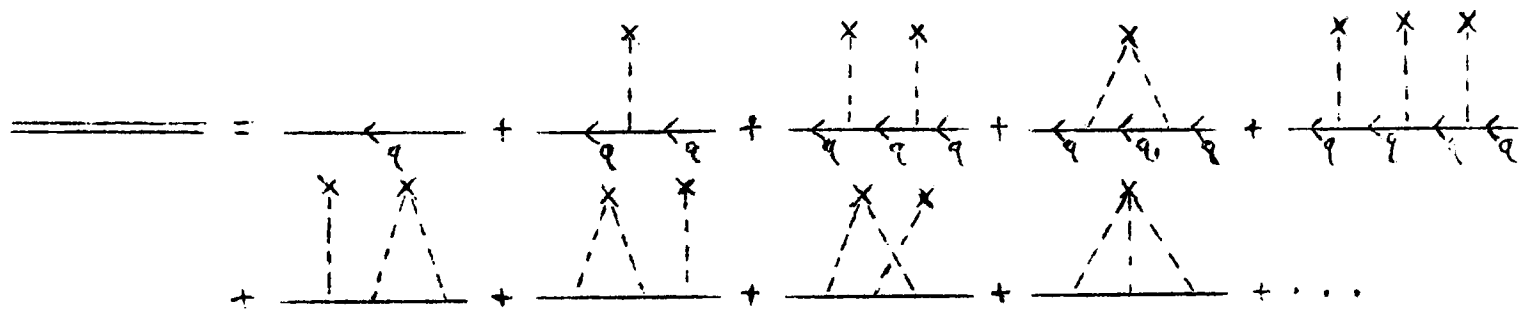
$$\langle V_{qq'} \rangle = c \frac{\epsilon}{1-\epsilon} \omega_q^2 \delta_{qq'}$$

$$\langle V_{qq_1} V_{q_1 q'} \rangle = \omega_q^2 \omega_{q'}^2 \left(\frac{\epsilon}{1-\epsilon}\right)^2 \left[\frac{c(1-c)\delta_{qq'}}{N} + c^2 \delta_{qq'} \delta_{qq_1}\right]$$

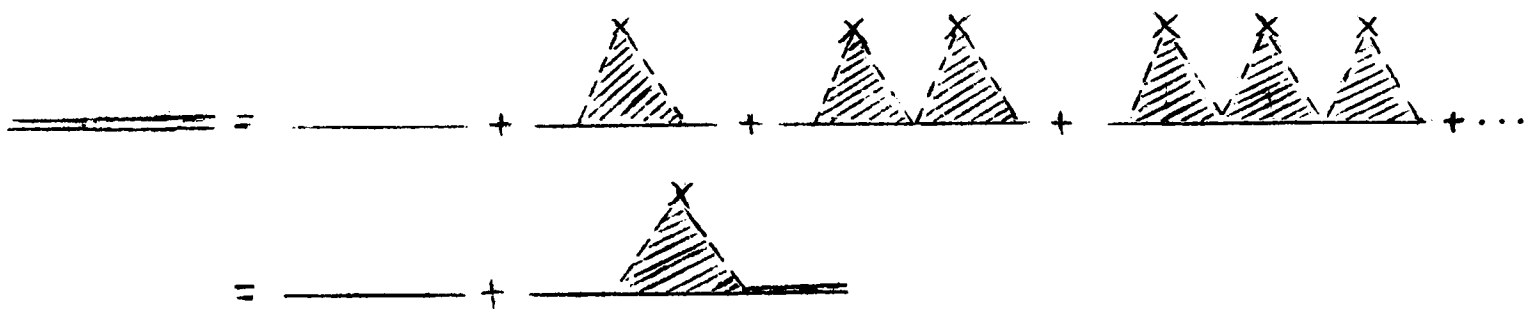
which we see are diagonal on q, q' . The result,

$$\langle G(\omega^2) \rangle_q = g_q + g_q \langle V \rangle_q g_q + g_q \sum_{q_1} \langle V V \rangle_{qq_1} g_{q_1} g_q + \cdots$$

can be written symbolically in terms of diagrams in which the perfect lattice propagator is represented by a solid horizontal line and the interaction with a defect site, X , by a dashed vertical line.

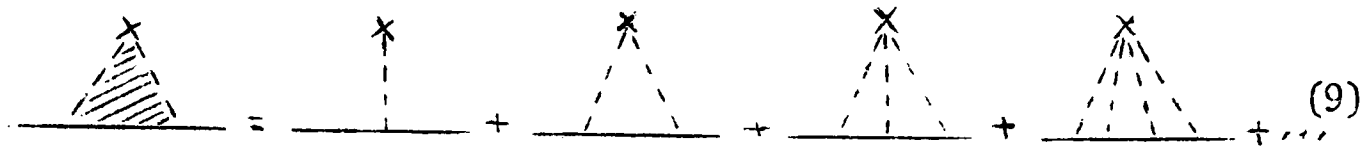


Of these diagrams, we need concern ourselves only with the types



(8)

where



(9)

and since all interactions at a single site are included, all terms linear in the concentration have been taken into account. Equation (8) can be written

$$\langle G(\omega^2)\rangle_q = \frac{1}{\omega^2-\omega_q^2} + \frac{1}{\omega^2-\omega_q^2}\sum(q,\omega)\langle G(\omega^2)\rangle_q$$

$$= \frac{1}{\omega^2-\omega_q^2-\sum(q,\omega)},$$

defining the self-energy, $\sum$. Since $\sum$ is given by (9), and is

$$\sum(q,\omega) = c\{\langle V\rangle_q + \langle VgV\rangle_q + \cdots\},$$

it is just the concentration times the T-matrix in q-space associated with a single defect. (We have followed Langer in neglecting the factor (1 - c) in $\langle V_{qq'}V_{q'q'}\rangle$, although Taylor retains it and arrives at a result which corresponds to $\delta\phi$ before the approximation is made in (7)).

Thus we arrive at (1), which gives a dispersion relation for the imperfect crystal, and can be used, like (7), to find the elastic constants.

What is essential to the self-energy approach is that it allows for multiple scattering of phonons by the defects. Thus the dispersion relation for an imperfect crystal contains terms to all orders in the concentration, and so will the elastic constants of the imperfect crystal as a result. On the other hand, the method of finding elastic constants by taking a configuration average of the force constants alone, $\langle \Phi + \varphi \rangle$, decoupled from the average of the strain, $\langle w \rangle$, leads to terms of order at most c^2 (Liu & Shimizu, 1967) in the harmonic approximation. This is because the most complicated situation that can arise, assuming forces between pairs of atoms only, involves two defects directly coupled together by overlapping force constant matrices, φ_i , (or two host atoms coupled together, which produces a term in $(1 - c)^2$). Furthermore, this result is not correct even to first order in concentration, because it does not include multiple scatterings from the same defect, an effect given by the denominator of the T-matrix. In the static or long-wave limit, the scattering of phonons is the same as the interaction of strains, and this is why both strains and force constants must be included in the configuration average to give the correct result.

We now give the results of this method for $CaF_2 : H^-$, on the same model as in the previous chapter - rigid ions, coupling in the perfect lattice with Coulomb forces and short range forces out to third neighbours, with defects coupling to the host lattice with altered

nearest neighbour and second nearest neighbour central forces.

The result of applying the long wave method to CaF_2 is (Sennett 1966)

$$C_{11} = -\frac{1}{r_0}\left[a+C+2c+4f\right] + 3.276\,\frac{Z^2}{r_0 v}$$

$$C_{12} = -\frac{1}{r_0}\left[2b-a-A+2e-d-c+4h-2g-2f\right] - 5.396\,\frac{Z^2}{r_0 v}$$

$$C_{44} = -\frac{1}{r_0}\left[a+A+d+c+2g+2f\right] - 1.527\,\frac{Z^2}{r_0 v} + \frac{\left(b+5.038\,\frac{Z^2}{v}\right)^2}{r_0(a+2A+C)}$$

where the lattice constant $2r_0 = 5.45\text{Å}$, $v = 2r_0^3$,

Z is the charge on the fluorine ion, and the other symbols stand for the various force constants which constitute ϕ , as in section IV.2. To find the change in the elastic constants, contributed by the T-matrix, we simply write

$$\Delta C_{11} = \frac{c}{r_0}\left[a_T + C_T\right]$$

$$\Delta C_{12} = \frac{c}{r_0}\left[2b_T - a_T - A_T\right]$$

$$\Delta C_{44} = \frac{c}{r_0}\left[a_T + A_T\right]$$

where the symbols subscripted T now refer to the elements of the T-matrix which are analogous to those of ϕ in the first set of expressions. The T-matrix only extends to second neighbours, and cannot cope with a change in the charge on the defect, since this produces an effect extending throughout the crystal. This introduces an error into the results, since we have shown in the previous section that the charge is indeed changed on the defect.

The results for $CaF_2 : H^-$, to first order in concentration, c, are

$$C_{11} = (1.74 - .585c) \times 10^{12} \text{ dyne/cm}^2$$

$$C_{12} = (0.56 + 0.266c) \times 10^{12} \text{ dyne/cm}^2$$

$$C_{44} = (0.359 - 0.364c) \times 10^{12} \text{ dyne/cm}^2$$

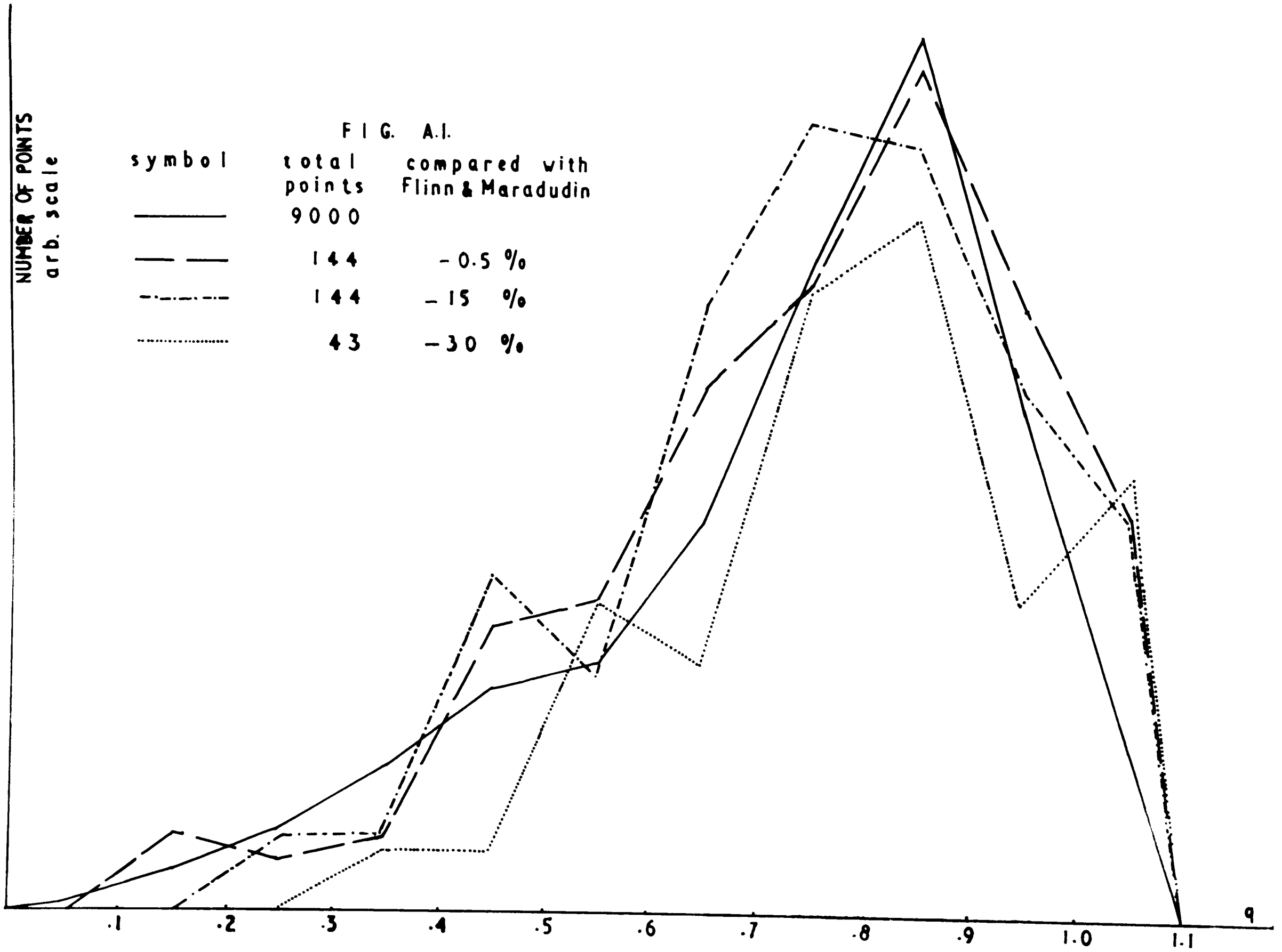
APPENDIX

On Calculating $g(\omega^2)$

The expressions (I.8) and (I.9) for the Green's functions required by the two parts of this thesis were evaluated on the EREAC computer at R.R.E., Malvern, where Dr. C.T. Sennett made available to us a magnetic tape containing a random selection of values of $\underline{q}$ together with the appropriate values of the Kellerman coefficients. Since the $\underline{q}$'s form a quasicontinuous distribution of $\sim 10^{23}$ points, we cannot sum over them all in (I.8) and (I.9). The usual approach is to sum over a subset which forms a regular mesh, and, in (I.9), in the volume enclosing $\underline{q}=0$, where $D^{-1}(\underline{q})$ has a pole owing to the vanishing of the acoustic mode frequencies, to evaluate g analytically. This can also be done in the random mesh, by taking special precautions to exclude all q-values within a certain radius of the origin from the discrete part of the sum. Then the contribution from the origin can be evaluated analytically without the danger of counting any points twice - a danger which is significant near the origin owing to the divergence there of the summand. However, this spoils part of the advantage of the random mesh, which is taken within the cube in the first octant, cornered at the origin, and ignores boundaries between Brillouin zones and between the $1/48^{th}$ of the zone that constitute the

FIG. A.I.

symbol	total points	compared with Flinn & Maradudin
———	9000	
— — —	144	-0.5 %
-·-·-·-	144	-15 %
·····	43	-30 %



symmetry-independent regions. The contribution from the sphere at the origin to the sum is linear in the radius,

$$\frac{1}{(2\pi)^3}\,\frac{1}{\Omega_{BZ}}\int_0^{q_0}\frac{4\pi q^2\,dq}{c^2q^2} = \frac{1}{(2\pi)^3}\,\frac{1}{\Omega_{BZ}}\,\frac{4\pi q_0}{c^2}$$

where $D^{-1}(q) = (cq)^{-2}$ and Ω_{BZ} is the volume of the Brillouin zone. Using this, it is easy to estimate from an examination of the distribution of q-values with $|q|$ the error arising from taking only the discrete part of the sum and neglecting analytic corrections from the origin. The distribution we employed, of 9000 values of q in $1/48^{th}$ of the Brillouin zone, varies as q^2 down quite close to the origin (see figure 1), and we can conclude that our computed values of g are accurate to within a value that is 1% of $g_{\alpha\alpha}\binom{0}{F}\binom{0}{F}$, where F stands for the fluorine site in (I.9). This conclusion is supported by a comparison of a special case of the computed results with those published by Flinn & Maradudin (1962) for a face-centred cubic Bravais lattice with central nearest neighbour coupling.

In the case of (I.8) the inclusion of the imaginary part of ω^2 makes unnecessary all these tactics. The computation was done for only 500 points in the $1/48^{th}$ Brillouin zone, as the numerical labour is considerably greater. (The distribution of these points is very similar to the 9000 point distribution of figure 1). The imaginary part, ϵ, must be chosen so that the "delta-function" in

$$\frac{1}{x+i\epsilon} = P\left(\frac{1}{x}\right) - i\pi\,"\delta(x)"$$

is narrow enough not to overlap with too many neighbouring "delta-functions", but broad enough that the resulting Green's functions are smooth functions of ω . For the number of q-values included it was considered that $\epsilon = .01\,\omega^2_{MAX.}$ would satisfy this compromise. Unfortunately because of the limitations of computer time, it was not possible to compare the effect of different values of ϵ .

The Green's functions that result from this computation are given below in units of 10^{-4} cm/dyne.

Calcium Fluoride. $\omega = 0$. The notation is that of section IV.2.

k =	.16866	A =	- .02582
l =	.26906	B =	.00838
a =	.07834	C =	- .15547
b =	.00678	α =	.01507
c =	.05165	β =	.00150
d =	.03723	γ =	.02043
e =	.01355	δ =	.00255
f =	.03002	ϵ =	.00215
g =	.04547	μ =	.02552
h =	.00814	λ =	.09323
x =	.00000		

Silicon R = 0. The notation is that of section I.4.

a) REAL

f	g^{11}	g^{12}	g^{22}	g^{13}	g^{23}	g^{33}
0.00	- .1404	.05663	- .04104	.8771	- .5630	- 13.05
0.02	- .1412	.05694	- .04119	.8827	- .5657	- 13.10
0.04	- .1434	.05792	- .04165	.8999	- .5740	- 13.26
0.06	- .1469	.05961	- .04244	.9298	- .5887	- 13.53
0.08	- .1516	.06212	- .04364	.9744	- .6107	- 13.95
0.10	- .1575	.06562	- .04534	1.0371	- .6421	- 14.55
0.12	- .1655	.07042	- .04770	1.1233	- .6857	- 15.37
0.14	- .1758	.07671	- .05090	1.2378	- .7452	- 16.50
0.16	- .1871	.08435	- .05508	1.3805	- .8238	- 18.01
0.18	- .1960	.09219	- .05994	1.5351	- .9183	- 19.88
1.0	- .06937	-.028450	- .000006	.01814	- .06204	- 2.012
1.1	.03531	-.014005	- .007310	- .01430	- .07379	- 2.308
1.2	.02430	-.009561	- .009493	- .01961	- .08031	- 3.121
1.3	.01843	-.007231	- .010625	- .01978	- .08492	- 3.305
1.4	.01471	-.005765	- .011333	- .01	- .08569	- 3.428
1.5	.01213	-.004752	- .011820	- .01702	- .09109	- 3.518
1.6	.01024	-.004008	- .012177	- .01546	- .09325	- 3.586

b) IMAGINARY

f	g^{11}	g^{12}	g^{22}	g^{13}	g^{23}	g^{33}
0.00	- .02862	.009065	- .003972	.1579	- .07260	- 1.369
0.02	- .02924	.009213	- .004029	.1604	- .07363	- 1.388
0.04	- .03122	.009680	- .004208	.1684	- .07684	- 1.447
0.06	- .03478	.010540	- .004536	.1830	- .08271	- 1.554
0.08	- .04015	.011930	- .005068	.2066	- .09222	- 1.727
0.10	- .04737	.014088	- .005908	.2432	- .10720	- 1.999
0.12	- .05730	.017506	- .007264	.3013	- .13124	- 2.432
0.14	- .07236	.023172	- .009545	.3979	- .17160	- 3.158
0.16	- .09579	.032757	- .013561	.5626	- .24273	- 4.436
0.18	- .13215	.049006	- .020850	.8467	- .37314	- 6.800

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